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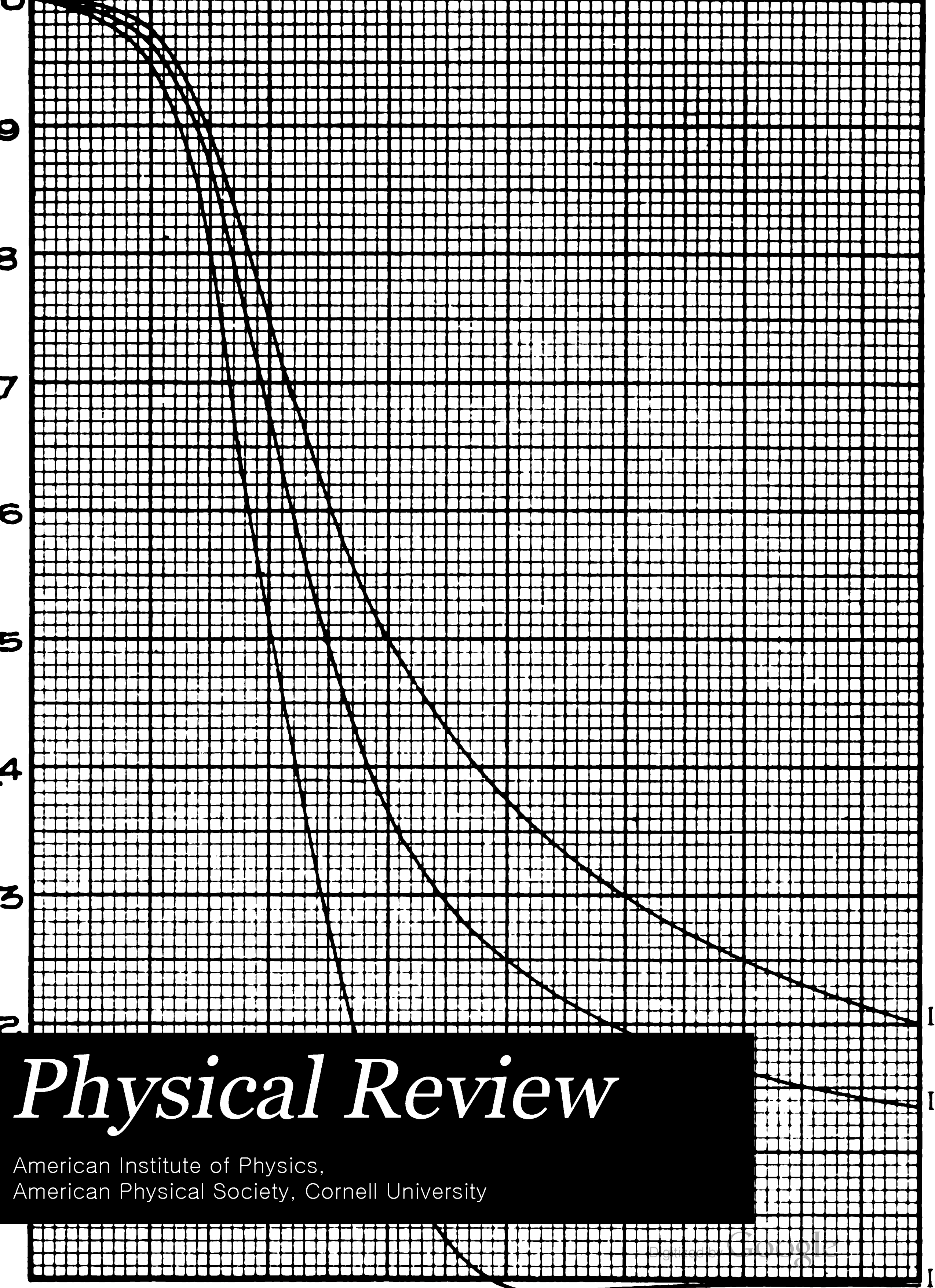

# Physical Review

American Institute of Physics,
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One of the Books of

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these, the movers of the world,
so still.

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# PHYSICAL REVIEW

*A JOURNAL OF EXPERIMENTAL AND THEORETICAL PHYSICS*

CONDUCTED WITH THE CO-OPERATION
OF THE
AMERICAN PHYSICAL SOCIETY
BY
EDWARD L. NICHOLS, ERNEST MERRITT,
AND FREDERICK BEDELL

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THE

PHYSICAL REVIEW.

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# THE REFLECTION OF CATHODE RAYS FROM THIN METALLIC FILMS.

By S. R. Williams.

## Introduction.

CATHODE rays after impingement upon a metallic surface may be considered from three standpoints: (1) Those rays which are reflected, (2) those which are absorbed or give up their charge to the metal, and (3) those which pass through if the metal is in thin enough layers. As to whether the rays reflected or those emerging from the rear side of a thin film are the identical ones which were incident upon the front surface is still an open question.

Among those having investigated the conditions of transmission and the properties of the transmitted cathode ray may be mentioned Hertz,[1] Lenard,[2] Leithaüser[3] and Des Coudres.[4] In a later research Lenard[5] studied the absorption of cathode rays in various media, on which subject Seitz[6] published some results at the same time. To our knowledge of the behavior of the reflected cathode ray, Swinton,[7] Starke[8] and Gehrcke[9] have made valuable contributions.

From these various researches two important conclusions may

[1] H. Hertz, Wied. Ann. 45, p. 28, 1892.
[2] Ph. Lenard, Wied. Ann. 52, p. 27, 1894.
[3] Leithaüser, Ann. d. Physik., 15, p. 283, 1904.
[4] Des Coudres, Physik. Zeitschr., 4, p. 140, 1902.
[5] Ph. Lenard, Ann. d. Physik., 12, p. 714, 1903.
[6] Seitz, Ann. d. Physik., 12, p. 860, 1903.
[7] Swinton, Proc. Roy. Soc., 64, p. 395, 1899.
[8] Starke, Ann. d. Physik., 5, p. 75, 1900.
[9] Gehrcke, Sitzber. d. k. Akad. d. Wissen. zu Berlin, 18, April, 1901.

be drawn: (1) With increasing potential, the transmission of cathode rays through a thin metallic film also increases; (2) the reflection coefficients remain constant for potentials ranging from 4,000 volts upward, if the reflectors are 1 mm. or more thick.

The transmission of cathode rays through thin metallic films shows that the rays penetrate the surface, but when we consider that the reflection coefficients of thick reflectors remain constant for varying potentials, the question arises, does reflection take place at the surface and thus remain constant in amount or do the rays which penetrate the surface suffer reflection from layers in the metal at depths which depend on the potential so that the amount reflected remains unchanged. If all reflection is from the front surface then reflection should be independent of thickness. If however deeper layers are also concerned it might be possible with increasing potential and very thin films to reach a critical point where a part of the rays would pass through and the reflection coefficient of the film be diminished. We might in the later case find for thin films a reflection coefficient diminishing with increasing potential.

To distinguish if possible between these two points of view of cathode ray reflection, the following study was undertaken at the suggestion of Professor E. Warburg and the experiments carried out in the physical laboratory of the University of Berlin.

## Methods of Investigation.

From the various researches that have already been made on the reflection and transmission of cathode rays it is evident that there are two methods available for such an investigation: (1) The electrical method in which the charge carried by the reflected rays is measured by a galvanometer. (2) The photometric method in which the fluorescent brightness produced by the reflected rays is taken as a measure of the quantity reflected.

The electric method was first tried and the form of apparatus as used by Starke[1] was adopted in which the charge given up by the absorbed rays was measured instead of the quantity which the reflected rays carry. According to Starke, if a quantity of electricity,

---

[1] Starke, Ann. d. Physik., 3, p. 97, 100.

$Q$, transported by cathode rays, falls on a metallic reflector which is connected to earth through a galvanometer, the current which the galvanometer shows is

$$I = Q(1 - r)$$

where $r$ is the reflection coefficient of the metal. Replacing one metal by another whose reflection is $r'$ and the current is

$$I' = Q(1 - r').$$

$Q$ remaining constant in both cases, we can write

$$I/I' = (1 - r)/(1 - r'),$$

whence follows

$$r' = 1 - (1 - r)I'/I. \qquad (1)$$

Thus if $r'$ be the reflection coefficient of a thin film and $r$ that of a plate of the same metal, then any variation in $r'$ would cause a change in $I'$ by which if $r$ was known $r'$ could be determined. Here $I'$ must include transmitted as well as absorbed charges.

In this way the reflection coefficient of a thin aluminum film about 1.5 $\mu$ was compared with an aluminum reflector, about 2 mm. thick, for the amount of cathode rays which they reflected. The reflection coefficient of the thick reflector was taken as 25 per cent., the value found by Austin and Starke.[1] Although comparisons were made at potentials as high as 18,000 volts no variations between the two currents $I$ and $I'$ could be detected. A d'Arsonval galvanometer with 10,000 ohms resistance being used to measure the currents. As higher potentials with the tube used gave inconstant readings, the results by the electrical method were in this case negative. These negative results however did not seem to be conclusive evidence. Since aluminum reflects 25 per cent., the other 75 per cent. given up to the reflector is measured by the galvanometer, hence a fairly large percentage variation in the amount reflected would have to occur before the variation would appreciably affect the galvanometer reading. Moreover this method offered no means of studying the loss in velocity of the rays reflected from thin films, which would be of especial interest here if any change in the amount reflected occurred.

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[1] Austin u. Starke, Ann. d. Physik., 9, p. 292, 1902.

On those grounds the electrical method was given up and the photometric method tried since it seemed to offer as great a sensibility and had the advantage that it was possible also to investigate the loss in velocity of rays reflected from thin films.

When cathode rays fall upon a fluorescent screen, the brightness of the illumination, $H$, will depend on the current density of the rays per unit area which falls on the screen, and some function of the potential under which the rays are produced, such as $H = [I \times f(V)]$, where $I$ represents the current density and $V$ the potential. This dependence of the brightness of fluorescence on the current density and the potential under which they are produced has been carefully worked out by Leithaüser.[1] From his data it appears that the brightness is approximately proportional to the current density of the rays falling upon the screen, while on the other hand, the dependence of brightness on the potential with constant current shows that this relation is not a linear function, but that the ratio $\frac{\text{Brightness}}{\text{Discharge Potential}}$ at first increases with increasing potential while at still higher potentials, the ratio again decreases. Hence when comparing two fluorescent spots produced by cathode rays, the discharge potential must be taken into account. From these relations worked out by Leithaüser, we can compare the current densities of cathode rays from any two sources, by knowing the relative brightness of the fluorescence produced when they impinge upon a screen, for

$$\frac{H}{H'} = \frac{(I)f(V)}{(I')f(V')},$$

thus $H/H' = w$, a ratio which may be determined by means of a photometer. From these quantities we then have

$$\frac{I}{I'} = w\frac{f(V')}{f(V)} \qquad (2)$$

where the ratio $f(V')/f(V)$ may be obtained from Leithaüser's tables.

The two sources of cathode rays just mentioned may be two reflectors, one of which is a thin aluminum film, whose reflection coefficient is to be investigated, the other being a thick aluminum reflector, whose reflection coefficient is known.

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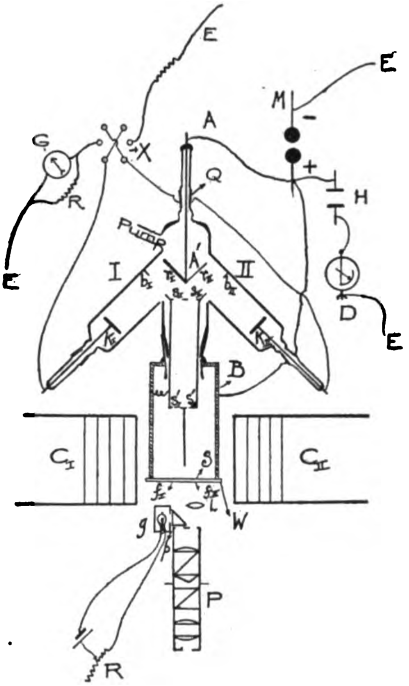
[1] Leithaüser, Ann. d. Physik., 15, p. 283, 1904.

If then rays of the same intensity fall on both reflectors, by the equation just given, we can determine the ratio of the quantities reflected, by knowing the ratio of brightness of the fluorescence and by the data given in the tables of Leithaüser. By allowing the rays reflected from these two sources to pass through narrow apertures, side by side, narrow and sharply defined fluorescent spots may be obtained on the screen, which, by means of a magnetic field, can be drawn out into magnetic spectra, parallel to each other, and comparison of the amounts reflected be made.



Fig, 1.

The final form of the apparatus as used is shown in Fig. 1. In general the apparatus resembled that used by Gehrcke,[1] only with changes to suit the present problem. The most noteworthy difference is that Gehrcke studied the reflected rays which had struck the reflector at an angle of 45°, in this work the rays were incident normally upon the reflectors.

The apparatus consisted of a bronze box, *B*, 19 cm. high, 6 cm. broad and 13 cm. in depth, which allowed for space in which the rays might be drawn out into parallel spectra. The rear side of the box was closed by means of a thick piece of plate glass, *W*. This plate carried the fluorescent screen which was made by sprinkling calcium sulphide on the thinnest possible layer of grease, rubbed over the inner surface of the glass plate. The advantage of the calcium sulphide as a fluorescent substance is, that the fluorescent after-glow dies away rapidly after the bombardment of the cathode particles has ceased, allowing measurements to be made in rapid succession on the same part of the screen. This property varies with the sample. Into a circular opening in the front side of the box, *B*, was sealed the discharge tube, which consisted of a main tube, 4 cm. in diameter, to which were joined two equal side tubes, *I* and *II*, 3 cm. in diameter, entering the main tube at an angle of 45°. These side tubes contained the cathodes $K_I$ and $K_{II}$, the faces of which were parallel to the reflectors, $r_I$ and $r_{II}$, and at a distance of about 8 cm. from them.

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[1] Gehrcke, Sitzber. d. k. Akad. d. Wissen. z. Berlin, 18, April, 1904.

For the production of the discharge current a 20-plate influence machine, *M*, of the Toepler type, was used. Its negative pole was earthed, while the positive pole was connected to the anode, *A*. The rod on which the reflectors, $r_I$ and $r_{II}$, were fixed, served as anode and since the metal cylinder containing the slits, $s_I$, $s_{II}$, $s_I'$ and $s_{II}'$, and the screens, $b_I$ and $b_{II}$, were within about 2 cm. of the reflectors, they were charged to the same potential as the reflectors, by metallic connection with the side of the box, *B*, and positive pole of the machine as shown. To work with high potentials, the box, *B*, was insulated on heavy glass plate to prevent leakage to earth through platform on which the apparatus was placed. The cathodes, $K_I$ and $K_{II}$, were then earthed to complete the circuit. The potential at the cathodes being almost zero, allowed the measuring of the cathode discharge with a galvanometer, *G*, without the disturbing influences of static charges under high potentials. The two cathodes were connected to a six-pole reversing switch, *X*, in such a way that first one cathode and then the other could be connected to earth through the shunted galvanometer, *G*, while simultaneously the other cathode was earthed through a resistance, *R*, equal to the resistance of the shunted galvanometer. If the current was the same in both side tubes, then the deflection of the galvanometer should be the same in both cases, a condition obtained in all final readings. Thus cathode rays passing out from the two cathodes, $K_I$ and $K_{II}$, fall on the reflectors, $r_I$ and $r_{II}$, respectively after having passed through horizontal slits 1 by 15 mm. in the screens, $b_I$ and $b_{II}$. From the two reflectors the rays are reflected diffusely in all directions and part of the rays from $r_I$ pass through the two horizontal slits, $s_I$ and $s_I'$ (1 by 6 mm. in size and in the same plane as the slit in $b_I$), and finally fall upon the fluorescent screen, $S$, producing the fluorescent spot, $f_I$. Similarly the rays from $r_{II}$ produce the fluorescent spot, $f_{II}$. $f_I$ and $f_{II}$ are then drawn out into magnetic spectra by means of the solenoids, $C_I$ and $C_{II}$,[1] and the spectral distribution of the rays measured.

It is at once apparent that this method will not give correct results unless the intensities of cathode discharge from $K_I$ and $K_{II}$ are equal. The elimination of such inequalities from the preliminary measurements was the cause of so much trouble that it may be useful to mention the precautions finally taken to prevent errors of this sort.

As may be seen from Fig. 1 the apparatus is symmetrical about an axis running through the anode, $A$, and the photometer, $P$. In putting the apparatus together, unless each part was symmetrically placed, inequality of the two currents in the side tubes occurred. Also when the two reflectors, $r_I$ and $r_{II}$, were of different metals, the currents were not the same. This was to be expected, as the reflector having the largest reflection coefficient produced a greater ionization in the discharge space and so more current passed through the side-tube which carried the reflector of largest reflection coefficient. In comparing copper and aluminum, for example, the reflection coefficient of copper is 45 per cent. and that of aluminum 25 per cent., a larger current always passed through the side-tube facing the copper reflector. This error was eliminated by placing between the cathodes and the reflectors the screens, $b_I$ and $b_{II}$, with narrow slits in them which prevented rays from the reflectors being thrown back into the discharge space to any appreciable amount.

An inequality of cathode discharge in the two branch tubes due to unavoidable dissymmetry of construction was still present and to eliminate this from the results the two reflectors, $r_I$ and $r_{II}$, were mounted on a shaft, $A'$, which could be rotated by means of the ground-glass joint, $Q$, through which the shaft passed. Any inequality of cathode discharge in either one of the branches could be eliminated by taking readings from both branches with the mirrors in one position and repeating with the mirrors reversed. This gave a mean which was free from errors of this sort. Any inequalities of size or position of the slits, or lack of uniformity in the fluorescent screen was also eliminated at the same time, as measurements were made of each reflector under exactly the same conditions as the other. A further inspection of the symmetry of the apparatus shows that the fluorescent spots, $f_I$ and $f_{II}$, could be compared directly with each other by means of the photometer[1] or by inserting a right-angled prism, $p$, over one opening of the photometer the brightness of either spectrum could be compared with the constant brightness of an incandescent lamp. The direct comparison of the two spots, $f_I$ and $f_{II}$, worked very well until high potentials were reached and then discharge would take place first through one side-tube and then the other in quick succession. For high potentials only one cathode was used and first one reflector and then the other was turned into position and the brightness of the spectra compared with the standard lamp, the current being held constant as shown by the galvanometer during the rotation of the reflectors.

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[1] S. Simon, Wied. Ann., 69, p. 595, 1899.

A Sprengel pump was used in exhausting the tube. As soon as an adequate vacuum was reached the pump was cut off and the occluded gases, driven from the cathodes by the discharge, were absorbed by cocoanut shell charcoal in a bath of liquid air according to Dewar's method.[2] This gave most satisfactory and constant results. By varying the opening between the tube and the receptacle holding the charcoal almost any pressure could be maintained for some considerable time, so that with the influence machine giving constant current very steady conditions were obtained.

The spectra formed on the fluorescent screen, when a magnetic field was produced, were focused by means of a lens, $L$, on the openings of the photometer, the image being natural size. By means of a faintly illuminated scale, the amount of deflection and dispersion, and the position of the photometer openings in the spectra were easily and quickly determined. Only those readings were accepted in which constant current conditions were maintained.

For convenience of observation, the length of spectra were divided into four regions and for each of the four positions of the photometer ten readings were made, during which both current and potential were held constant. The fourth region was generally too faint in illumination to be measured. Thus sixty readings were necessary to determine one reflection coefficient for a single potential, as the two spectra had to be separately compared, region by region, with the standard lamp. On repeating such a set of readings it was found that from 6 to 7 per cent. accuracy could be obtained.

---

[1] F. F. Martens, Phys. Zeitschr., 1, p. 299, 1900.

[2] J. Dewar, Compt. Rendus, 139, p. 261, 1904.

Having the apparatus to all appearances free from errors it was of interest to compare this method with the electrical method used by Starke.[1] Accordingly a comparison of the reflection coefficients of copper and aluminum was made. The reflection coefficients of these two metals Starke determined by direct methods and afterwards verified his results by a comparative method, hence their values were pretty well fixed.

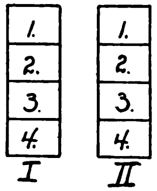

Fig. 2.

If we divide the two magnetic spectra to be compared into sections as shown in Fig. 2, by knowing the ratio of the brightness of the various sections we can determine the relative current densities of cathode rays producing the spectra, from the equation,

$$\frac{I_I}{I_{II}} = \frac{n_1 + n_2 k_1 + n_3 k_2 + n_4 k_3}{1 + k_1 + k_2 + k_3} + \cdots \qquad (3)$$

where the $n$'s represent the ratios of brightness between sections having the same deflection, here indicated by sections having the same number. These ratios are read directly from the photometer as we are comparing cathode rays of the same potential and the brightness in such a case Leithaüser has shown is directly proportional to the current density of rays producing the fluorescence. The $k$'s are ratios of the intensities of the cathode rays between 1 and 2, 1 and 3, 1 and 4, etc., determined by equation (2). The $k$'s were always measured in the brightest spectrum which in this case was that of copper. If

$$n_1 = n_2 = n_3 = n_4$$

then the distribution throughout the two spectra is the same and

---

[1] Starke, l. c.

$$I_I / I_{II} = n.$$

This means that the ratio of brightness of the two undeflected spots for the condition of equal distribution in the two spectra is the same as the ratio of the reflection coefficients.

The undeflected spots, $f_I$ and $f_{II}$, were 5 mm. wide and somewhat longer and when the magnetic field was on, these were drawn out into spectra a little over 15 mm. long. The width of the photometer openings were also 5 mm. so that lengthwise of the spectra there were three sections 5 mm. wide that could be measured. Increasing the magnetic field lengthened the spectra but decreased the brightness, so that a spectrum 18 to 20 mm. in length was found the most advantageous in use.

The distance from the centers of the undeflected spots to the centers of the various sections was taken as the deflection of that section. The potential of section 1, was taken as the potential at which the rays were produced since rays which come direct from cathode without reflection would be deflected by this amount as shown by Gehrcke.[1] Of course with such wide photometer openings as those used in the present work the rays producing the fluorescence on the two sides of the opening would of course correspond to different potentials, but by considering the brightness observed in each region as that belonging to the center, we get a fair average, although not an absolute value. Any such error was still further reduced when two equally deflected sections of neighboring spectra were compared.

In a magnetic spectrum the deflection, $z$, varies inversely as the velocity of the rays, $v$. But the velocities stand in the same ratio as the square roots of the potentials, so that we may write $z^2 \propto 1/V$. For the various sections of the spectra, $z$, could be measured, and the potential and deflection of section 1 being known, the corresponding potential for the others could be determined.

Since the reflection coefficients of massive metal plates remain constant for varying potentials, to compare the coefficients of aluminum and copper, a potential of 16,500 volts was chosen, as at this potential a very steady current could be maintained. The data obtained in this photometric comparison are given herewith and graphically shown in Fig. 3, where the current densities are plotted as ordinates, and abscissas as distances from center of section 1, $z_0$ being the magnetic deflection of section 1.

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[1] Gehrcke, Sitzber. d. k. Akad. d. Wissen. z. Berlin, 18, April, 1901.

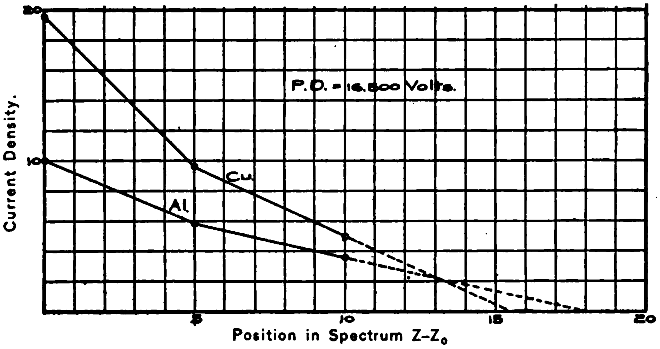

Fig. 3.

| | | | |
|---|---|---|---|
| Deflection of section | (1) 1.7 cm. | (2) 2.2 cm. | (3) 2.7 cm. |
| Voltage " " | (1) 16,500 | (2) 9,850 | (3) 6,550 |
| Corresponding brightness | (1) 182.6 | (2) 110.1 | (3) 56.4 |
| (Interpolated from the tables of Leithaüser.)[1] | | | |
| Measured brightness | (1) 0.601 | (2) 0.178 | (3) 0.044 |

$1_{al}/1_{cu} = n_1 = 0.518.$ $2_{al}/2_{cu} = n_2 = 0.616.$ $3_{al}/3_{cu} = n_3 = 0.787.$

(These ratios were also photometrically measured.)

$$\frac{0.178}{0.601} \times \frac{182.6}{110.1} = k_1 = 0.491, \quad \frac{0.044}{0.601} \times \frac{182.6}{56.4} = k_2 = 0.337.$$

$$\frac{I_I}{I_{II}} = \frac{n_1 + n_2 k_1 + n_3 k_2}{1 + k_1 + k_2} = \frac{0.518 + (0.616 \times 0.491) + (0.787 \times 0.237)}{1 + 0.491 + 0.237}$$

$$= \frac{1.006}{1.728} = 0.58,$$

the ratio of the reflection coefficients of aluminum and copper. Austin and Starke[2] found as the value for this ratio, 0.56 which, considering the accuracy of 6 to 7 per cent. which this method afforded, is a fair agreement. The results showed that the apparatus was in working order and free from large errors. The copper reflector was replaced in succession by a series of thin aluminum films and the properties of the rays reflected from them compared with the reflection from a thick aluminum plate. The first film used was 0.53 $\mu$ thick, the thickness being measured with a Zeiss Dickenmesser. Ten and twenty thicknesses of the aluminum leaf were laid together and the total thickness divided by the number gave results agreeing to 0.01 $\mu$. The thickness was not over 0.53 $\mu$ although it might possibly have been thinner as some allowance must be made for the air layers between the leaves. This error was made as small as possible however by pressing the films firmly together in measuring.

---

[1] Leithaüser, Ann. d. Physik., 15, p. 296, 1904.

[2] Austin u. Starke, Ann. d. Physik., 9, p. 292, 1902.

On comparing the brightness of fluorescence produced by the rays reflected from a thin and a thick aluminum reflector at higher potentials, viz., about 20,000 volts, the difference was so great as to be readily observed with the naked eye.

Since the reflection coefficient of the films varied for potentials above a critical potential, it was necessary to measure the entire spectrum for each potential used. The first film was measured at the potentials 11,000, 16,500, 21,800 and 27,750 volts. For these high potentials it was necessary to connect a condenser in series with the Braun electrometer, *D*, as shown in Fig. 1, as the range of the electrometer, was from 4,000 to 10,000 volts only. This worked satisfactorily as long as the atmosphere in the room was dry. If it was not, whenever the influence machine was short-circuited, a charge would remain on the electrometer due to leakage over the glass supports.

The observations were made in the same order as in the comparison of aluminum and copper already described and the results are given in the following tables and curves:

Potential = 11,000 volts.

| | | | |
|---|---|---|---|
| Deflection of section | (1) 2.3 cm. | (2) 2.8 cm. | (3) 3.3 cm. |
| Voltage of section | (1) 11,000 | (2) 7,400 | (3) 5,350 |
| Corresponding brightness | (1) 129.0 | (2) 66.6 | (3) 43.6 |
| Measured brightness | (1) 1.83 | (2) 0.478 | (3) 0.197 |

$$n_1 = 1.021, \quad n_2 = 0.958, \quad n_3 = 0.949.$$

$$\frac{0.478}{1.83} \times \frac{129.0}{66.6} = k_1 = 0.505.$$

$$\frac{0.197}{1.83} \times \frac{129.0}{43.6} = k_2 = 0.318.$$

$I_I=$ total quantity in spectrum from thin film.

$I_{II}=$ total quantity in spectrum from thick film.

$$\frac{I_I}{I_{II}}=\frac{n_1+n_2k_1+n_3k_2}{1+k+k_2}=\frac{1.021+(0.958\times 0.505)+(0.949\times 0.318)}{1+0.505+0.318}$$

$$=\frac{1.807}{1.823}=0.991=\frac{x}{25},$$

where 25 per cent. is the amount reflected by the thick reflector. That is, 0.991 is the ratio of the reflection coefficients of the thin and thick aluminum reflectors at a potential of 11,000 volts. This means that within the accuracy of the method the two reflectors are equal. (See Fig. 4.)

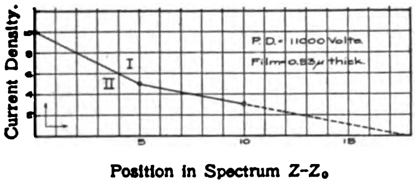

Fig. 4.

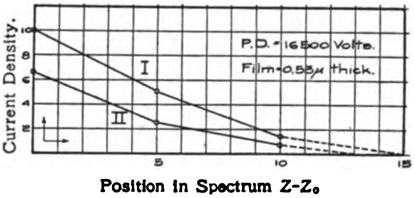

Fig. 5.

Potential = 16,500 volts.

| | | | |
|---|---|---|---|
| Deflection of section | (1) 2 cm. | (2) 2.5 cm. | (3) 3 cm. |
| Voltage of section | (1) 16,500 | (2) 10,550 | (3) 7,350 |
| Corresponding brightness | (1) 182.6 | (2) 122.2 | (3) 66.0 |
| Measured brightness | (1) 2.65 | (2) 0.868 | (3) 0.130 |

$$n_1=0.656,\quad n_2=0.517,\quad n_3=0.451.$$

$$\frac{0.868}{2.65}\times\frac{182.6}{122.2}=k_1=0.489.$$

$$\frac{0.130}{2.65}\times\frac{182.6}{66.0}=k_2=0.135.$$

$$\frac{I_I}{I_{II}}=\frac{0.656+(0.517\times 0.489)+(0.451\times 0.135)}{1+0.489+0.135}$$

$$=\frac{0.970}{1.624}=0.597=\frac{x}{25}.$$

$x=14.9$ per cent. reflected at a potential of 16,500 volts. (See Fig. 5.)

Potential = 21,800 volts.

| | | | |
|---|---|---|---|
| Deflection of section | (1) 1.8 cm. | (2) 2.3 cm. | (3) 2.8 cm. |
| Voltage of section | (1) 21,800 | (2) 13,350 | (3) 9,000 |
| Corresponding brightness | (1) 195.0 | (2) 161.5 | (3) 95.8 |
| Measured brightness | (1) 3.57 | (2) 0.98 | (3) 0.25 |

$$n_1 = 0.518, \quad n_2 = 0.274, \quad n_3 = 0.216.$$

$$\frac{0.98}{3.57} \times \frac{195.0}{161.5} = k_1 = 0.331.$$

$$\frac{0.25}{3.57} \times \frac{195.0}{95.8} = k_2 = 0.142.$$

$$\frac{I_I}{I_{II}} = \frac{0.518 + (0.274 \times 0.331) + (0.216 \times 0.142)}{1 + 0.331 + 0.142}$$

$$= \frac{0.640}{1.473} = 0.434 = \frac{x}{25}.$$

$x = 10.8$ per cent. reflected from the thin reflector at a potential of 21,800 volts. (See Fig. 6.)

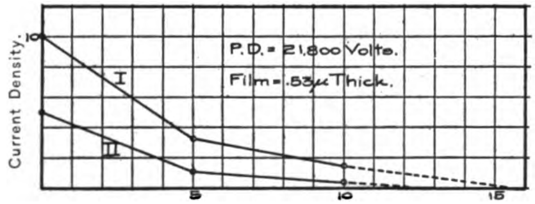

Fig. 6.

Potential = 27,750 volts.

Section (3) of the spectrum from the thick reflector was so faint in intensity that no measurements could be taken, as were also (2) and (3) of the spectrum from thin film.

| | | |
|---|---|---|
| Deflection of section | (1) 1.5 cm. | (2) 2 cm. |
| Voltage of section | (1) 27,750 | (2) 15,600 |
| Corresponding brightness | (1) 225.5 | (2) 179.4 |
| Measured brightness | (1) 3.06 | (2) 0.239 |

$$n_1 = 0.329.$$

$$\frac{0.239}{3.06} \times \frac{225.5}{179.4} = k_1 = 0.096.$$

$$\frac{I_I}{I_{II}} = n_1 = 0.329 = \frac{x}{25}.$$

$x = 8.22$ per cent. reflected at the potential of 27,750 volts from a thin film. (See Fig. 7.) From the above results the reflection coefficients of an aluminum film, 0.53 $\mu$, may be plotted as a function of the potential. (See Fig. 12.)

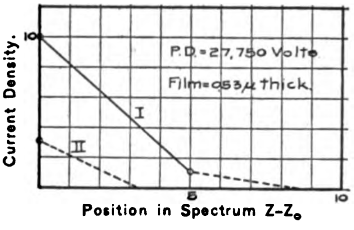

Fig. 7.

Next the reflection of an aluminum film, 1.90 $\mu$, was measured as described above. The results follow:

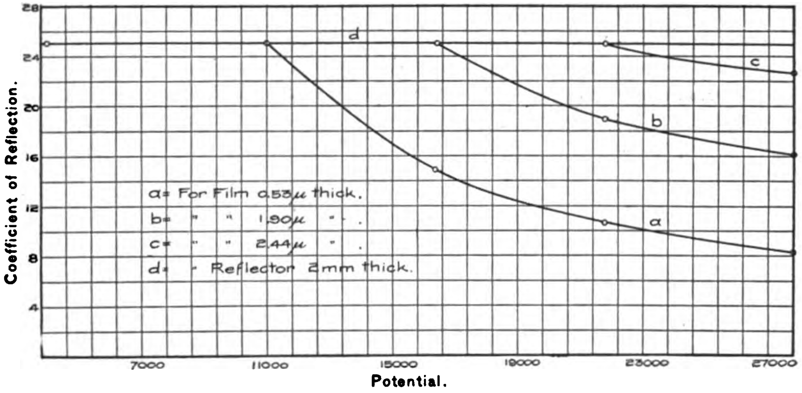

Fig. 12.

| | | | |
|---|---|---|---|
| Potential = 16,500 volts. | | | |
| Deflection of section | (1) 2.1 cm. | (2) 2.6 cm. | (3) 3.1 cm. |
| Voltage of section | (1) 16,500 | (2) 10,750 | (3) 7,600 |
| Corresponding brightness | (1) 182.6 | (2) 125.2 | (3) 69.7 |
| Measured brightness | (1) 2.99 | (2) 0.736 | (3) 0.245 |

$$n_1 = 1.023, \quad n_2 = 0.978, \quad n_3 = 0.934.$$

$$\frac{0.736}{2.99} \times \frac{182.6}{125.2} = k_1 = 0.358.$$

$$\frac{0.245}{2.99} \times \frac{182.6}{69.7} = k_2 = 0.214.$$

$$\frac{I_I}{I_{II}} = \frac{1.023 + (0.978 \times 0.358) + (0.934 \times 0.214)}{1.572} = \frac{1.572}{1.572} = 1.00 = \frac{x}{25}.$$

$x = 25$ per cent. reflected from film $1.9\,\mu$ thick at a potential of 16,500 volts. The reflection is the same as a thick reflector. (See Fig. 8.)

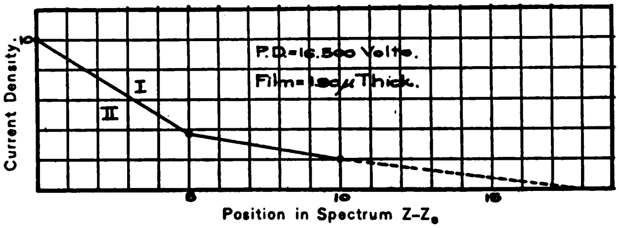

Fig. 8.

Potential = 21,800 volts.

| | | | |
|---|---|---|---|
| Deflection of section | (1) 1.8 cm. | (2) 2.3 cm. | (3) 2.8 cm. |
| Voltage of section | (1) 21,800 | (2) 13,350 | (3) 9,000 |
| Corresponding brightness | (1) 195.0 | (2) 161.5 | (3) 95.8 |
| Measured brightness | (1) 4.58 | (2) 0.574 | (3) 0.225 |

$$n_1 = 0.796, \quad n_2 = 0.710, \quad n_3 = 0.555.$$

$$\frac{0.574}{4.58} \times \frac{195.0}{161.5} = k_1 = 0.151.$$

$$\frac{0.225}{4.58} \times \frac{195.0}{95.8} = k_2 = 0.099.$$

$$\frac{I_I}{I_{II}} = \frac{0.796 + (0.710 \times 0.151) + (0.555 \times 0.099)}{1.250}$$

$$= \frac{0.958}{1.250} = 0.767 = \frac{x}{25}.$$

$x = 19.2$ per cent. reflected at potential of 21,800 volts. (See Fig. 9.)

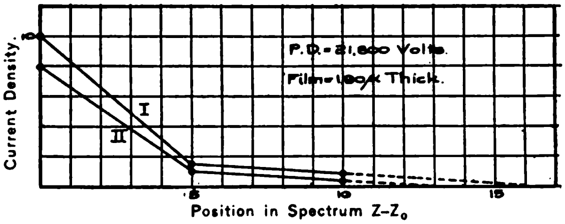

Fig. 9.

Potential = 27,750 volts.

| | | |
|---|---|---|
| Deflection of section | (1) 1.5 cm. | (2) 2.0 cm. |
| Voltage of section | (1) 27,750 | (2) 15,600 |
| Corresponding brightness | (1) 225.5 | (2) 179.4 |
| Measured brightness | (1) 4.41 | (2) 0.441 |

$$n_1 = 0.671, \quad n_2 = 0.510.$$

$$\frac{0.441}{4.41} \times \frac{225.5}{179.4} = k_1 = 0.125.$$

$$\frac{I_I}{I_{II}} = \frac{0.671 + (0.510 \times 0.125)}{1.125} = \frac{0.735}{1.125} = 0.653 = \frac{x}{25}.$$

$x = 16.3$ per cent. reflected at this potential of 27,750 volts. (See Fig. 10.) Just as for the previous film, so here we can plot the reflection coefficients as a function of the potential. (See Fig. 12.)

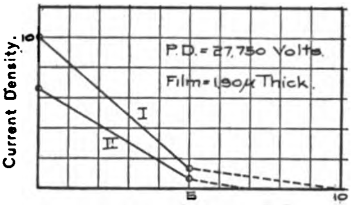

Fig. 10.

Finally the reflection of an aluminum film 2.44 $\mu$ thick was compared with a massive plate for potentials of 21,800 and 27,750 volts. At the lower potential, plate and film reflected equally. The results for 27,750 volts follow :

| | | |
|---|---|---|
| Deflection of section | (1) 1.5 cm. | (2) 2.0 cm. |
| Voltage of section | (1) 27,750 | (2) 15,600 |
| Corresponding brightness | (1) 225.5 | (2) 179.4 |
| Measured brightness | (1) 3.61 | (2) 0.640 |

$$n_1 = 0.947, \quad n_2 = 0.756.$$

$$\frac{0.640}{3.61} \times \frac{225.5}{179.4} = k_1 = 0.222.$$

$$\frac{I_I}{I_{II}} = \frac{0.947 + (0.756 \times 0.222)}{1.222} = \frac{1.114}{1.222} = 0.911 = \frac{x}{25}.$$

$x = 22.7$ per cent. reflected from a film 2.44 $\mu$ thick at a potential of 27,750 volts. (See Fig. 11.) For the curve of reflections plotted as a function of the potential, see Fig. 12.

Having thus found a variation of reflection with thickness for aluminum, it seemed of interest to measure the reflection coefficients of thin films of other metals. In place of the aluminum reflectors a thick copper reflector and a copper film 0.66 $\mu$ thick were compared. For the highest potential, viz., 27,750 volts no difference in reflection was found. Since the gradient of brightness in a spectrum reflected from copper is large as compared with aluminum, the spectra were so short that measurements could only be made in the first section, so that

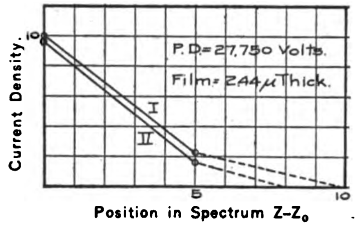

Fig. 11.

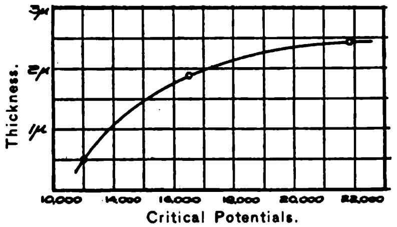

Fig. 13.

$$\frac{I_I}{I_{II}} = 1.002 = \frac{x}{45}, \quad x = 45.0$$

for a copper film 0.66 $\mu$ thick and at a potential of 27,750 volts. Thus there is a marked difference in behavior of thin aluminum and thin copper films.

If we plot as shown in Fig. 13 the thickness of aluminum films used, as a function of the potential at which the reflection begins to diminish we find that the curve rises quite rapidly to a point between 1.90 $\mu$ and 2.44 $\mu$ and then becomes more nearly parallel to the axis of abscissas. It thus appears that for reflectors 1 mm. thick it would take an infinite potential before any of the reflected rays would be lost by transmission. In other words this would be saying that whatever the potential, the reflected rays are never from a depth greater than 1 mm.

## Discussion of Results.

From the data just given, we are in a position to discuss some of the conditions under which the reflection of cathode rays take place, especially when reflected from thin films.

The question as to whether the reflection of cathode rays from metals occurs at the surface or whether there is penetration and then reflection has been answered by the results in such a way as to leave no doubt but what the rays penetrate to various depths, depending on the potential, and are then reflected. In the beginning it was assumed that a part of the cathode rays, which would be reflected from a thick film, would in the case of a thin one be lost by transmission after a critical potential was reached and so a thin film would not show as large a reflection as a thick one. The results substantiate this view in that a difference in the quantities reflected, depending on thickness and potential, was found. This dependence of reflection upon potential and thickness will here be discussed more in detail.

For the film 0.56 thick at a potential of 11,000 volts the reflection coefficients of the thin and the thick reflectors are the same. At 11,000 volts then the critical potential has not been reached. On increasing the potential however, a difference occurs, and the only way the decrease in the amount reflected from the thin film can be accounted for is that a part has been lost by transmission. This indicates then that the reflection is not all taking place at the surface of the reflectors, but that there is penetration and then reflection for some of the rays. Although at 11,000 volts the thin film did reflect as much as a thick one, this is not saying that none of the cathode rays passed through the thin film, for behind the film a fluorescence on the walls of the tube showed that some of the rays were coming through, thus some rays penetrate even farther than those reflected from the greatest depths. At the same potential, viz., 11,000 volts, and with a film 1.8 $\mu$ thick, Leithaüser[1] still found some transmission.

Again the data and the curves show that there is a decrease in the quantity of rays reflected as one goes from rays of less to those of greater deflection in the magnetic spectrum, further the difference in brightness of corresponding sections of the two spectra is greatest in the most deflected portions, *i. e.*, from equation (3) $n_3 < n_2 < n_1$. This is in accord with what has just been said concerning the reflection of rays which have penetrated to greater depths and which have been slowed down in consequence. Take a case where a difference in reflection from the two reflectors occurs. Those rays which are penetrating farther into the thick film than the thickness of the thin one are being thrown out and form a large part of the most deflected portion of the spectrum. Consequently the difference in brightness of the most deflected portion of the two spectra will be greater than in the less deflected part, because in the case of the thin film the larger part of those rays which form the most deflected part of spectrum have been lost by transmission, and so we find there the greatest difference in brightness between the two spectra. Fig. 11 illustrates the point in question. The difference in brightness of the least deflected portions of the two spectra is so small that it might pass as an error in the reading. In the next section of the two spectra however a much larger difference occurs, showing that for that part of spectrum from the thin film, a part of the rays has been lost by transmission.

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[1] Leithaüser, Ann. d. Physik., 15, p. 305, 1904.

The penetration of cathode rays into copper is interestingly shown by the results given on page 18 where a thin and a thick copper reflector are compared. Here the penetration of the reflected rays is very much less than in aluminum. For a potential of 27,750 volts the penetration of the reflected rays in copper must be less than 0.66 $\mu$ as this thickness reflected as much as a plate 2 mm. thick. With an aluminum film and the same potential, viz., 27,750 volts, the penetration of the reflected rays was about 2.5 $\mu$ as curve 9 shows. Fig. 3 and the results given in the comparison of the amounts reflected from thick reflectors of aluminum and copper, show that the reflection, in the case of copper must take place nearer the surface of the reflector as the difference in brightness between corresponding sections of the spectra measured was greatest in the least deflected portions, for $n_1 < n_2 < n_3$, that is, the larger part of the rays from the copper reflector were being reflected without appreciable loss of velocity. The spectrum from the copper reflector was also noticeably shorter in length than the one from aluminum. As one approached the more deflected portions of the spectra therefore, the ratio between the brightnesses approached unity. The values given also indicate this, viz.,

$$n_1 = 0.518, \quad < n_2 = 0.616 < n_3 = 0.787.$$

That Gehrcke[1] did not find so great a difference in the spectra of the rays reflected from copper and aluminum is quite likely due to the fact that he was not using normal incidence of the rays in his work.

Sufficiently thin films of other metals with known reflection coefficients could not be obtained, but from the data given above for copper and aluminum, and the fact that Starke[2] found an increasing reflection coefficient the greater the density of the metal, would lead one to infer that the denser the material of the reflector, the less the penetration of the reflected rays.

## SUMMARY OF RESULTS.

1. The reflection of cathode rays does not all take place at the surface of a metal, but there is penetration and then reflection for a large part of the reflected rays.

2. From a critical potential on, a thin metallic film of aluminum reflects less than a thick one since a part of the rays have been lost by transmission.

3. This decrease in the amount reflected from a thin film appears first in the most deflected rays and with increasing potential will also be found in the least deflected portion.

4. The critical potential depends on the thickness and the nature of the film. For aluminum this critical potential for thicknesses $0.56\mu$, $1.90\mu$ and $2.44\mu$ is 11,000, 16,500 and 21,800 volts respectively. For a copper film of thickness $0.66\mu$, the critical potential has a value greater than 27,750 volts.

5. The foregoing data has shown a fair qualitative agreement with the theory deduced by Professor E. Warburg,[3] although the values given do not show the desired agreement with those calculated.

In conclusion the writer takes pleasure in acknowledging his indebtedness to Professor E. Warburg, under whose direction the foregoing work was undertaken, for many kindnesses and helpful suggestions throughout the course of the experiments.

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[1] Gehrcke, l. c.

[2] Starke, l. c.

[3] Theories on the reflection of cathode rays have been given by Professor E. Warburg, Verhandl. d. Deut. Physik. Gesell., VI. Jahrg., Nr. 1; J. Stark, Phys. Zeitschrift, 3, p. 161, 1901; J. J. Thomson, Conduc. of Elec. Through Gases, p. 509.

# ON THE PHYSICAL PROPERTIES OF FUSED MAGNESIUM OXIDE.

By H. M. Goodwin and R. D. Mailey.

IN connection with a recent note from the Königlichen Porzellan Manufaktur[1] on the manufacture of tubes, crucibles, etc., of pure oxide of magnesium, we have thought that the results of various experiments which we have recently made on the physical properties of this substance after it has been actually fused, may prove of some interest.

Our attention was first directed to the preparation of fused oxide of magnesium in an attempt to find a substance which at temperatures up to at least 1000° C. would serve as suitable containing vessels for fused salts in an investigation now in progress on their electrical conductivity, *i. e.*, a substance which would possess the properties of being chemically inert, a nonconductor of electricity, and having a sufficiently high melting point to retain its shape at the temperatures mentioned. A small coefficient of expanson was also desired. We were particularly desirous of obtaining tubes or rods of such a substance. Whether the material described by the Charlottenburg firm is magnesia which has actually been fused or not is not quite clear. It seems highly improbable, however, that tubes of the fused material 80 cm. long and 7 cm. in diameter and crucibles 50 cm. high and of any diameter have been made. These are probably moulded under pressure from powdered magnesia and then heated to a high temperature.

After experimenting with a number of silcates and metallic oxides, both in the natural crystalline form and artificially prepared, in the hopes of finding a satisfactory material, it was decided to try to make pure fused magnesium oxide. That this should be possible in the electric furnace seemed probable, as Moissan states that the carbide is not formed when the oxide is heated with carbon. The first attempt was made in a graphite-resistance furnace. A pure Acheson graphite rod, 18 inches long and ¾ inch outside diameter, was bored with a ½-inch drill and the ends fixed into large graphite block terminals for leading in and out the current. The furnace was mounted vertically, packed with coke to prevent excessive oxidation of the graphite tube and the whole heat-insulated with fire brick. The furnace was heated by current from a 50 kw. transformer, the voltage of which could be varied by steps of 10 volts from 160 volts to 10 volts. From 20–30 kw. were used in the furnace to maintain the temperature required. Chemically pure magnesium oxide was fed in at the top of the furnace in the form of powder and packed down by means of a graphite rod. In this way it could be melted and rods of the fused oxide were obtained about one fourth inch in diameter and two inches long.

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[1] Zeitschrift für Electrochemie, *11*, 581, 1905.

In no case, however, could rods be formed as large as the interior diameter of the bored graphite rod, owing to an action between the oxide and either of the walls of the tube, or gases given off from or diffusing through the walls of the enclosing tube. This was indicated by the formation of a volatile product which condensed to a black mass in the upper cooler portions of the furnace. To prevent this substance from completely stopping up the furnace it was found necessary to bore lateral holes through the graphite tube in the hottest zone, at which condensation could not take place. The composition of the substance condensed in the cooler part of the furnace was not determined, although tests indicated that it was not a carbide. Treated with acid, hydrogen sulphide was always evolved showing that impurities from without the furnace proper, probably in the coke, must have diffused through the graphite to the oxide within. The graphite rods were tested and found to be very pure, having been especially prepared for this work through the kindness of the Acheson Graphite Co., of Niagara Falls.

As it was found that rods of magnesia of the desired size could not be obtained by the method above described (at least when carried out on the scale feasible at the time), it was thought that an arc furnace might be more effective. A hollow rectangular graphite boat, 10 × 4 × 4 cm., was used as a receptacle for the fused oxide.

Over the center of this was arranged a powerful alternating current arc into which the oxide was fed from above. The whole was enclosed in graphite bricks, around which were built up fire bricks. In this way irregular masses of the fused oxide, as large as one's hand, were obtained; and from such masses, rods or pieces of the desired size were bored by means of carborundum. The large masses thus obtained were not, however, homogeneous. Certain portions or layers were composed of very fine compact crystals resembling marble, other portions were composed of larger crystals. Some excellent samples were obtained, however, so hard and compact that they were quite non-porous to water and to fused salts. The great difficulty experienced was in getting pieces sufficiently free from minute bubbles or blow holes. Up to the present time we have been unable to completely eliminate these in pieces larger than two or three cubic centimeters. If the process were to be carried out on a much larger scale and a larger mass of oxide brought to a state of quiet fusion and then cooled, better results could undoubtedly be obtained.

## Physical Properties.

*Appearance.* — The fused oxide when pure and uncontaminated with particles of graphite is a pure white, very hard crystalline substance. The fused surface resembles glazed porcelain. Depending upon the rapidity of cooling the crystals appear either very minute and compact, giving the structure the resemblance of marble, or fairly large and compactly arranged in layers. The substance takes on a good polish.

*Hardness.* — The fused oxide is exceedingly hard. Its hardness was found to be between that of apatite, transparent variety, and feldspar, white cleavable variety, being somewhat nearer the former than the latter.

*Specific Gravity.* — This was determined by the Archimedes method for a number of selected samples and the following values obtained:

| | |
|---|---|
| Sample *A*. Mean value of three small cylinders used for expansion experiments (see below). | 3.485 at 19° C. |
| Sample *B*. Mean value of large cylinder 5.5 cm. × 1.2 cm. diam. | 3.562 at 20° C. |
| Sample *C*. Mean value of four small irregular pieces. | 3.432 at 20° C. |
| Mean of *A*, *B*, *C*. | 3.493 at 20° C. |

The specific gravity of the mineral periclase consisting of crystalline magnesium oxide and a little ferric oxide, of the percentage composition:

| MgO | FeO |
|---|---|
| 93.86 | 5.97 |
| 93.38 | 6.01 |

is given as 3.674.

*Melting Point.* — The melting point was determined by putting two or more small fragments of the already fused oxide into a graphite tube resistance furnace, holding the current in the furnace constant, and determining the temperature of that part of the tube where the samples were placed by means of an optical pyrometer. If, after a run, the pieces were found to be fused together, the melting temperature was considered to have been exceeded. Thus by making a number of runs, temperature limits were determined between which the melting point lay.

The furnace consisted of a 11″ graphite tube, 1″ in diameter and bored out to ⅝″ inside diameter. Midway between the ends was a ⅝″ hole, opening laterally into the bore of the tube. The ends of the tube were attached to graphite terminal blocks, 6″ square and 3″ thick. The opening in which the sample to be fused was placed was viewed through a larger hollow graphite tube placed at right angles to the furnace tube. To prevent too rapid oxidation of the furnace the tube was surrounded with fine coke and magnesia powder which was held in place by fire bricks and asbestos. By this arrangement when the furnace was heated the pyrometer could be sighted through the horizontal side tube at the opening in the heating tube and the conditions for "black body" radiation were approximately approached. In this furnace temperatures from 1500° to 2500° could be maintained with currents ranging from 300 to 700 amperes. The desired regulation of the current was obtained by an adjustable rheostat in the field of a 25 kw. low voltage D.C. generator.

The temperatures were measured with a Wanner pyrometer which had been calibrated at the Reichsanstaldt. This pyrometer had a range from 900° C. to 2000° C. which could be increased to 4000° C. by means of an auxiliary smoked glass screen.

The samples whose melting points were determined were fragments of magnesium oxide which had been previously fused. In every measurement the samples were placed near the side opening in the furnace tube, so that they were in line with the pyrometer. By this means the temperature of the graphite tube with which the samples were in contact was the temperature measured.

From the series of measurements made it was found that below 1890° C. the fragments did not fuse together or soften. Above 1940° C. they always fused together. This indicates that the melting point of magnesium oxide (fused) is between 1890° C. and 1940° C. In round numbers 1910° C. may therefore be taken as the approximate melting point of the oxide.[1]

*Electrical Conductivity.* — The electrical conductivity of the fused oxide was determined as follows:

A small cylinder, 8 mm. thick by 14 mm. in diameter, was first prepared by very carefully grinding its surface. This was placed between two pieces of thin platinum foil (*A*) which were pressed against the sample (*B*) by graphite rods (*C*). These were held in an iron frame as shown in Fig. 1. The upper graphite rod was insulated at the top by a piece of fused magnesium oxide (*D*) whose resistance was maintained practically infinite by keeping it outside of the furnace and consequently cool. To insure nearly constant pressure on the sample (*B*) during the heating, a lever (*E*) and spring (*F*) were used as shown. The whole arrangement of this apparatus was freely suspended from an insulated stand in a vertical cylindrical electric furnace of the platinum resistance type. The 110- or 220-volt circuit was connected to the graphite rods (*C*) by means of platinum leads.

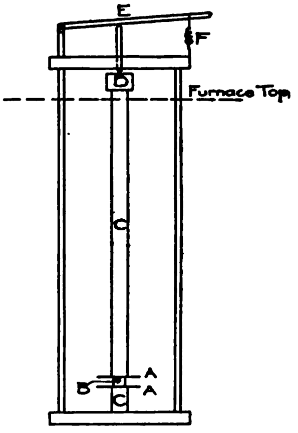

Fig. 1.

The sample to be tested and the graphite rods were connected in series with a Weston voltameter across the 110- (or 220-) volt D.C.

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[1] We hope shortly to fix the melting point of this and a number of other refractory oxides with a higher degree of precision than here attempted.

mains. The resistance under investigation being very much greater than the resistance of the voltameter itself (15,800 ohms), the latter could be used as an ammeter and deflections for a constant applied voltage assumed proportional to the current. Hence, if

$R$ = resistance of sample,
$R_v$ = resistance of voltameter = 15,800 ohms,
$V$ = reading with voltameter alone in circuit, *i. e.*, the voltage across mains,
$v$ = reading with voltameter + magnesia sample in series,

then

$$R = \frac{R_v(V - v)}{v}.$$

The temperature was measured by a thermoelectric junction, (platinum, platinum-rhodium), which was calibrated at the sulphur, aluminum, and gold points.

The values of the specific conductivity of the magnesium oxide in reciprocal ohms at various temperatures are given in Table I. and on the accompanying plot, Fig. 2. These values should be considered as maximum values, as slight traces of graphite remained in the sample in spite of the fact that it was heated repeatedly to near its melting point.

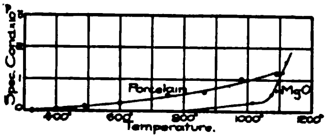

Fig. 2.

For comparison, the conductance of samples of Berlin and Meissen porcelain (glazed) were also measured in the above apparatus, and the values obtained are given in Table II. and on the same plot. The results show that magnesium oxide is a much better insulator than porcelain at temperatures below 1100° C. Above that temperature the large temperature coefficient of the oxide indicates that its conductivity probably becomes greater than that of porcelain.

Our measurements, which were made with direct currents, indicated distinct polarization in the case of porcelain but with the oxide no trace of such action was evident.

## Table I.

### Specific Conductivity of Fused Magnesium Oxide.

| Temperature. | Specific Conductivity. | Temperature. | Specific Conductivity. |
|---|---|---|---|
| 700° C. | | 1050° C. | $0.34 \times 10^{-6}$ |
| 800 | $0.01 \times 10^{-6}$ | 1100 | 1.00 " |
| 900 | 0.10 " | 1150 | 2.60 " |
| 1000 | 0.20 " | [1500[1] | $85. \times 10^{-6}$] |

## Table II.

### Specific Conductivity of Porcelain.

| Observed Values. | | | Values by: | |
|---|---|---|---|---|
| Temp. | Berlin. | Meissen. | Foussereau.[2] | Nernst,[3] Reynolds. |
| 50° C. | | | $0.465 \times 10^{-15}$ | |
| 200 | | | $0.746 \times 10^{-10}$ | |
| 400 | $0.05 \times 10^{-6}$ | $0.05 \times 10^{-6}$ | | |
| 500 | 0.20 " | 0.10 " | | |
| 600 | 0.32 " | 0.18 " | | |
| 700 | 0.43 " | 0.24 " | | |
| 800 | 0.55 " | 0.40 " | | |
| 900 | 0.75 " | 0.70 " | | |
| 1000 | 1.00 " | 0.94 " | | $3 \times 10^{-5}$ |
| 1100 | 1.30 " | 1.27 " | | |

*Coefficient of Expansion.* — This was determined by Mr. G. W. Eastman[4] by the Fizeau method, using the latest form of Abbé-Fizeau dilatometer, manufactured by the Zeiss Optical Co., of Jena. The interference apparatus was similar to that used by Reimedes, and consisted of two quartz plates, *A* and *B*, cut perpendicular to the optic axis. The samples of fused magnesium oxide used consisted of three small carefully ground cylinders, *D*, 7.4 mm. long and 2.5 mm. in diameter, which served to support the upper quartz plate upon the lower as shown in Fig. 3. These supports were placed at the vertices of an equilateral triangle. The interference fringes were produced between the upper surface of *B* and under surface of *A*. The coefficient of expansion of *D* could be at once computed from the measured shift of the fringes due to a measured change in temperature.

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[1] Nernst and Reynolds, Landolt and Börnstein's Tables.

[2] Landolt and Börnstein.

[3] Landolt and Börnstein.

[4] Thesis Mass. Inst. of Technology, 1904.

The heater consisted of a massive casting of copper so bored that the interference apparatus could be placed at the center and observed by means of a total reflecting prism from the outside side. The temperatures were measured by a very carefully calibrated platinum resistance thermometer, and extended over a range from 120° C to 270° C. The value for the linear coefficient of expansion over this range of temperature was found to be

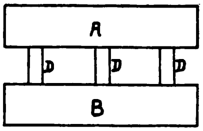

Fig. 3.

$$\alpha_t = 10^{-8}[1{,}140 + 0.92(t - 120^\circ)].$$

This value is not much greater than that for quartz crystal cut parallel to its optic axis and is nearly equal to that of platinum, as will be seen by comparison with the following data:

*Quartz Crystal.*

Randall,[1] $\alpha_t = 10^{-8}[717.0 + 1.620t]$ for temperatures to 250° C.

$\alpha_t = 10^{-8}[1{,}125.0 + 165(t - 250) + 0.00566\,(t - 250)^2 + 0.0000134(t - 250)^3]$ for $t = 250^\circ$ to $t = 470^\circ$.

Reimerdes,[2] $\alpha_t = 10^{-8}[692.5 + 1.689t]$ for $t = 5^\circ$ to $t = 220^\circ$.

Eastman,[3] $\alpha_t = 10^{-8}[698.7 + 1.580t]$ for $t = 85^\circ$ to $t = 235^\circ$.

*Fused Quartz.*

Holborn & Henning,[4] $\alpha = 54.0 \times 10^{-8}$ for $t = 0^\circ$ to $t = 1000^\circ$.

*Platinum.*

Holborn & Day,[5] $\alpha = (8{,}889 + 1.274t)10^{-9}$ for $t = 0^\circ$ to $t = 1000^\circ$.

Le Chatelier,[6] $\alpha = 1130 \times 10^{-8}$ for $t = 0^\circ$ to $t = 1000^\circ$.

[1] Physical Review, *20*, 10, 1905.

[2] Inaug. Diss., Jena, 1896.

[3] Thesis Mass. Inst. Tech., 1904.

[4] Ann. der Phys., *4*, 446, 1903.

[5] Ann. der Phys., *2*, 508, 1900.

[6] Landolt & Börnstein's Tables.

The close agreement between the value of the expansion coefficient of fused magnesia and that of platinum should prove a valuable property in the construction of apparatus involving joints of these two materials. We have found in fact that platinum caps ground to fit the ends of rods of the fused oxide remain tight over wide ranges of temperature.

*Heat Conductivity.* — The heat conductivity has not been determined in this laboratory. In a recent table of thermal conductivities of refractory materials published by Messrs. Hutton & Beard,[1] however, "Magnesia (fused)," is included, the conductivity of this material in the form of granular powder (600 meshes per sq. cm.) being given as $K = 0.00047$ as compared with $K = 0.00029$ for lime, and $K = 0.00028$ for fire brick. No details regarding the preparation of the magnesia are given by the authors.

*Chemical Properties.* — Fused magnesium oxide possesses in a remarkable degree the ability to withstand chemical action of many neutral salts at high temperatures, and is therefore well adapted for use as vessels and apparatus for containing such salts when subjected to high temperatures. Qualitative tests of the chemical action of various fused salts on the oxide gave the following results.

Silver, sodium and potassium nitrates, sodium and potassium chlorides, bromides and sulphates, zinc chloride and barium nitrate showed no action on a polished sample of the fused oxide when the latter was heated for an hour or more in the fused salt. Barium chloride had a very slight action; sodium carbonate, potassium sodium carbonate, potassium hydrate and cryolite attacked the fused oxide energetically.

Dilute hydrochloric, nitric and sulphuric acids attack the fused oxide in the cold slowly. Concentrated acids are less active than dilute acids.

Electrochemical Laboratory,
Massachusetts Institute of Technology.

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[1] Proceedings of the Faraday Society, I., 266, 1905.

# DISTRIBUTIONS OF COLLOIDAL NUCLEI AND OF IONS IN DUST-FREE CARBON DIOXIDE AND IN COAL GAS.

By C. Barus.

1. *Apparatus.* — The following experiments were made with the apparatus used in my last experiments[1] with dust-free air. The conveyance tubes between the exhaustion chamber (5 feet long and 1 foot in diameter) and the condensation chamber (18 inches long and 5 inches in diameter) were about 18 inches long and 2 inches in diameter. The rapid exhaustion thus secured is effective, but may not have reached a limit;[2] there is still too much resistance in the connecting pipes. The data obtained with such an apparatus are comparable with each other, and nothing further than this is aimed at, since in view of the very high exhaustions needed the constants for the computations of the absolute nucleations would in any case be lacking. It is a matter of convenience however, to compute the data at the high exhaustion as if the conditions met with at the low exhaustion were indefinitely applicable, and this is the meaning to be given to $n$, the number of nuclei per cubic centimeter, in the present paper. Moreover $n$ refers to the nucleation left in the *exhausted* fog chamber, supposing that the nuclei are restored to the gas faster than they can be withdrawn by exhaustion or that the nucleation encountered is fixed for any definite environment. Otherwise $n$ (to be multiplied by the volume expansion) would be very much larger.

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[1] Physical Review, XXII., pp. 105 et seq., 1906.

[2] The $\delta p$ in the text is the value observed under isothermal conditions at the fog chamber, the latter being isolated at once after exhaustion from the vacuum chamber. It will be shown elsewhere that this is much too high and that the true $\delta p$ must be computed from the initial pressures in fog and vacuum chambers and their common pressure when in communication, all at the same temperature. It is then found that a limit of efficiency has in fact been reached and is not inferior to any other apparatus.

The carbon-dioxide used was generated from calc-spar and hydrochloric acid. The gas was eventually passed through a solution of sodic hydro-carbonate, a long tube of dry bicarbonate of soda, a solution of silver nitrate and a calcium chloride drying tube. Then it entered a filter (two feet long) from which it was conveyed very slowly into the fog chamber.

Coal gas taken from a gas pipe was treated in the same way.

2. *Data for Carbon Dioxide.* — In the chart $\delta p$ shows the drop of pressure on exhaustion, the nucleation being obtained from $s/30$ (approximately) the angular diameters of the coronas, when the eye is at 30 cm. in front, and the source of light 250 cm. behind the fog chamber. The meaning of the other data is obvious, $n$ being the nucleation.

In the early parts of the work the exhaustion $\delta p$ was usually kept constant with the object of observing the behavior of the mixture of gases beginning with air and terminating with $CO_2$. About 8 exhaustions were found to lead to the steady behavior of the latter gas. Inasmuch as the original air was still present to the extent of about one per cent. and admixture of this amount may be regarded as inappreciable. In the succeeding parts of the experiments even 4 exhaustions, reducing the air content to but eleven per cent., nevertheless brought out the behavior of $CO_2$. Moreover, on readmitting air, two exhaustions nearly suffice to restore the air corona. Coronas for a given mixture are definite, being reproduced after several hours.

The relatively small coronas obtained with $CO_2$ as compared with air for the same drop in pressure and in the same apparatus, gave rise to a suspicion that water nuclei associated with HCl gas might be involved. In special experiments, therefore, atmospheric air was bubbled through HCl and the gas then passed through the same drying train. After three exhaustions exceptionally high air coronas were obtained, showing that the method of producing the gas is here of no consequence, thorough washing presupposed.

The chart gives a sufficient exhibit of the experiments with non-energized $CO_2$. The gas was then ionized by the X-rays, with the bulb at a distance of 200 cm., and the experiments continued in the same way. The usual constancy of corona at high exhaustions was observed. The fog limit again lies in a region of exceptionally high exhaustion as compared with air.

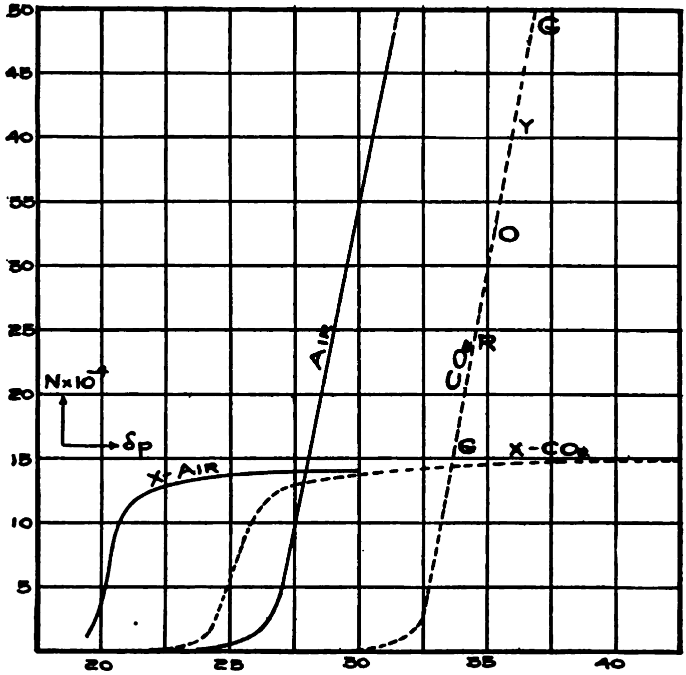

Fig. 1.

3. *The Behavior of Carbon Dioxide.* — The graphs are given in connection with the corresponding earlier data for air, both for the non-energized and the energized state. In both cases the curves are essentially similar in their contours, but the $CO_2$ curves require much higher exhaustion ($\delta p$), throughout, than the air curves. In other words the same coronas occur in $CO_2$ as in air, provided that in the former gas all the pressure differences are chosen to about 5 to 5½ cm. higher than in the case of air. Similar relations hold for the fog limits as was found directly by Wilson[1] in a small apparatus.

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[1] C. T. R. Wilson, Phil. Trans. Royal Soc., volume 189, page 288, etc., 1897. Wilson's fog limits are smaller than suggested above because of his apparently more efficient apparatus. They would agree with those of the text if $\delta p$ in the latter case were computed as already specified.

The peculiar feature of these results is the degree of parallelism of the $CO_2$ and air lines both for the non-energized and to a somewhat smaller extent for the energized state. The representative nuclei lie on curves of the same slope. Clearly the phenomena in both cases are alike in character though lying far apart on the chart.

4. *Cause of Differences.* — In view of the more coercible character of $CO_2$, one would naturally expect larger colloidal nuclei than in the case of air, and it was with this anticipation that the data were investigated. Taken at their full value, however, they would point to a conclusion exactly the reverse of this. The colloidal nuclei in $CO_2$ are apparently smaller than in the air, and the same is true, caet. par., for the ions.

Unfortunately the precise meaning of these results is not clear: for in the first place the amount of adiabatic cooling may be written in the usual notation,

$$\log \tau_0/\tau = (\gamma - 1)/\gamma \cdot \log p_0/p,$$

and thus between two fixed pressures

$$\log \tau_0/\tau = \text{const.}\ (\gamma - 1)/\gamma.$$

The value of this fraction is for air, .29; for $CO_2$, .22; for coal gas, .19. In other words the amount of cooling is less in $CO_2$ than in air under like conditions and hence the reduced efficiency of the fog chamber in the former case is qualitatively compatible with the thermal properties of $CO_2$ gas.

Quantitatively, however, this compensation does not seem to be sufficient. For instance, the same corona is obtained in air and $CO_2$ when the pressure difference is 28 cm. and 33.5 cm. respectively. For *like nuclei* this would imply the same degree of supersaturation. Hence if $p_1$ and $p_2$ be the vapor pressures of water before (20° C.) and after exhaustion, and $p = 76$ and $p - \delta p$ be the corresponding pressures, the occurrence of like supersaturation implies that

$$\frac{p_1}{p_2}\left(\frac{p - p_2 - \delta p}{p - p_1}\right)^{\gamma} = \frac{p_1}{p_2}\left(\frac{p - p_2 - \delta p'}{p - p_1}\right)^{\gamma'},$$

where $p'$ and $\gamma'$ refer to $CO_2$ and where $\gamma$ is the heat ratio for air.

Hence

$$\frac{\gamma}{\gamma'}=\frac{\log(1-(\delta p'+p_2)/p)-\log(1-p_1/p)}{\log(1-(\delta p+p_2)/p)-\log(1-p_1/p)},$$

where the value for $\gamma/\gamma' = 1.10$ as derived for direct experiment.

To compute the value of the same ratio from the coronal experiment it is necessary to know $p_2$, the vapor pressure on exhaustion and before condensation ensues. This datum is unavailable; but it must be greater than zero and less than would correspond to the decidedly lower exhaustion, $\delta p = 17$ cm., than the one applied ($\delta p = 28$ cm.). Hence limits of the value of $\gamma/\gamma'$ may be computed by inserting $p_2 = 0$ and $p_2 = .2$ respectively. The results are $\gamma/\gamma' = .128$ both for the superior and inferior limits, as would be otherwise anticipated.

One may summarize these results as follows. Either the heat ratio of carbonic acid, $\gamma'$, decreases in comparison with that of air, $\gamma$, very rapidly as temperature decreases, so that an average value of $\gamma/\gamma' = 1.3$ instead of $\gamma/\gamma' = 1.1$ is to be used in the preceding experiments; or all the colloidal nuclei in $CO_2$ though distributed in a way closely recalling that of air, are throughout smaller; at least there is no evidence showing that the colloidal nuclei of a coercible gas like $CO_2$ are larger than the colloidal nuclei of air. The adequacy of the first hypothesis is improbable since the same $\gamma/\gamma'$ would hold for ionized nuclei and for colloidal nuclei, though the phenomena appear in widely different regions of exhaustion. Similarly no suggestion would be offered for the close parallelism of the air and the $CO_2$ curves throughout their extent. Finally the phenomenon should be accentuated for coal gas where $(\gamma-1)/\gamma$ is smaller, but this is not the case.

5. *Data for Coal Gas.*—These were investigated in the same way as in the preceding case both for the non-energized and for the energized gas, when the X-ray bulb was at a distance of 200 cm. from the fog chamber. The measurements were much less satisfactory than the above, the corona being thin and blurred. As in case of $CO_2$ the data for coal gas throughout lie in a region of relatively low pressure, *i. e.*, large sudden reductions of pressure are needed to produce the coronas. Fog limits are correspondingly high—

all of which is again qualitively in keeping with the low heat ratio, $\gamma'$.

Apart from this the new results with the hydro-carbon gas in the earlier experiments differed thoroughly from the character of the results for air and $CO_2$. In the non-energized gas the nucleations rose with the pressure difference at a rapidly accelerated rate and this continued to the highest values of $\delta p$ applied, and long after the air and $CO_2$ nucleations had become stationary in the given apparatus.

Similarly for the weakly energized gas, the increase of nucleation was very gradual and the asymptote was scarcely reached within the interval, $\delta p = 40$ cm., of the experiment. All this was sharply in contrast with the rapidity with which air and $CO_2$ approach their respective asymptotes as may be seen by inspecting the chart.

In the final experiments, however, where care was taken to have the exhaustion chamber as well as the fog chamber full of dust-free coal gas, the behavior both for the highly energized and the non-energized states approached that of the other gases in character. The non-energized curves lay between those for air and $CO_2$, and in the energized gas the highest nucleations were producible.

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PROVIDENCE, R. I.

# STUDIES IN LUMINESCENCE.

By Edward L. Nichols and Ernest Merritt.

## VII. Further Experiments on the Decay of Phosphorescence in Sidot Blende and Certain Other Substances.

IN the two preceding papers of this series[1] experiments were described in which the phosphorescence of Sidot blende was followed by the spectrophotometer for about ten seconds after the cessation of excitation. At the end of this period the intensity of phosphorescence had fallen to about four per cent. of its original value. Although it was possible to see the phosphorescent light in the spectrophotometer for a much longer period than this, the extreme faintness of the field made accurate measurements out of the question. In attempting to determine the law of decay throughout a wider range we have therefore been compelled to abandon the use of the spectrophotometer and to measure the total light.

Measurements of the total intensity do not, in general, afford a satisfactory means of determining the law of decay of phosphorescence, since the phosphorescence spectrum usually contains two or more bands, which decay at different rates. We have already referred to the difficulties that are met with in interpreting the results of such measurements. In the case of Sidot blende the conditions are, however, relatively simple, for the phosphorescence of the green band is so much more prominent, both in duration and in intensity, than that of the violet bands that the presence of the latter does not appreciably affect the total intensity. Measurements of the total phosphorescence of Sidot blende are therefore practically measurements of the intensity of the green band only. If all parts of this band decay at the same rate, measurements of total intensity will give the same results as measurements taken at some particular portion of the band. Our earlier observations have shown that all parts of the green band of Sidot blende do decay at the same rate for at least ten seconds. It seems not unlikely, therefore, that this equality of rates will be maintained.

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[1] Physical Review, Vol. 21, p. 247, 1905; Vol. 22, p. 279, 1906.

Although the present paper deals chiefly with the phosphorescence of Sidot blende the results obtained in the study of several other substances are also included.

## EXPERIMENTAL METHOD.

The apparatus used is shown in Fig. 38. The white screen was removed from a Lummer-Brodhun photometer and the Sidot blende screen, *s*, was put in its place, the active surface of the screen being toward the left. The screen was usually excited by a Lummer mercury lamp, *L*, of the "end on" form. In some instances the carbon arc, and in other cases the spectrum of the carbon arc, was used for excitation. The exciting light could be cut off by means of a shutter, *S*, which at the same time made a record on a chronograph. When the mercury lamp was used in excitation a piece of blue glass, *B*, was placed between the lamp and the screen, so that only the violet lines in the spectrum were used.

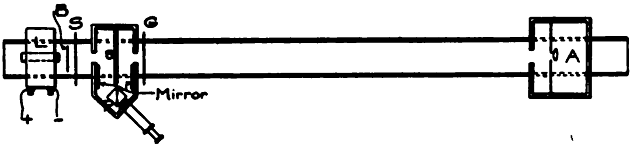

Fig. 38.

The right-hand side of the screen as seen in Fig. 38 was of white paper and could be illuminated by means of the acetylene lamp, *A*. Two pieces of green glass, *G*, served to produce a sufficient color match. The acetylene flame, *A*, was in a metal box, and the light used emerged from a small opening immediately in front of the central part of the flame. Small changes in pressure were therefore without effect upon the intensity of this comparison source.

The procedure in taking observations was as follows:

One observer, with his eyes suitably protected from stray light, watched the decay of the phosphorescence after the shutter had been closed, and recorded by means of a key the instant at which the phosphorescent light and the comparison field were equal. The second observer then shifted the position of the comparison flame, $A$, to a slightly greater distance from the photometer, and the time when equality was again reached was recorded as before. In this way it was often possible to get as many as fifteen points on the curve of decay, although a smaller number than this was more usual.

## EXPERIMENTS WITH SIDOT BLENDE.

In preliminary experiments the light from the carbon arc was used in excitation. It was thought that simpler conditions would be obtained if exciting light having only a small range of wave-lengths was used, and a spectrum of the arc was therefore formed, the violet end of which was used for excitation. The gain in the intensity of phosphorescence which resulted from cutting off the red and infra-red rays was very noticeable.

In our previous experiments with Sidot blende it was found that the decay of phosphorescence during the first seven seconds was in accordance with the law

$$I = \frac{1}{(a + bt)^2},$$

so that upon plotting the curves with $T$ and $I^{-\frac{1}{2}}$ as coördinates a straight line was obtained. Since the distance between the photometer screen and the acetylene flame is proportional to $I^{-\frac{1}{2}}$, it was convenient to plot the results of the present experiments in the same way.

The general character of the decay curves when plotted in this manner is exhibited by the curves of Fig. 39. The violet end of the carbon arc spectrum was used in excitation, and the duration of excitation was varied as indicated.

Inspection of Fig. 39 shows that while each curve starts as a line which is nearly straight in the neighborhood of origin, it soon begins to bend over and ultimately changes into a second straight line having a different slant. This behavior is especially noticeable in the case of long exposures.

If phosphorescence is due to the recombination of ions that have been separated by the action of the exciting light, as assumed in the theory of Wiedemann and Schmidt discussed in our last paper, it appears that the coefficient of recombination does not remain constant during the whole period of decay. During the first six or seven seconds this coefficient is practically constant, as was shown by the results of our previous experiments. A change then begins which continues for about twenty or thirty seconds, after which the curves indicate a new coefficient, smaller than before. This new coefficient, as is shown by the constant slant of the curves of Fig. 39, remains constant during the rest of the period of decay, or at least until the phosphorescence has become too faint to measure.

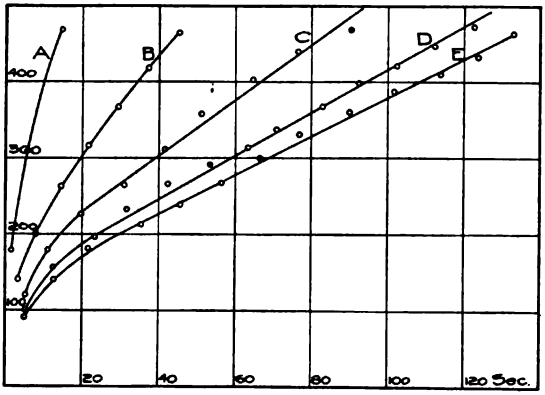

Fig. 39. Effect of duration of excitation. Violet end of carbon-arc spectrum used in excitation. The curves were taken in the order indicated by the letters. The times of excitation were as follows :

Curve *A*, 0.9 sec.
" *B*, 2.4 sec.
" *C*, 4.5 sec.
Curve *D*, 9.2 sec.
" *E*, 17.5 sec.

Whatever theoretical interpretation of the curves is adopted it is clear that the decay of phosphorescence involves two distinct processes which merge into one another. In each of these the decay obeys the simple law already referred to, but the rate at which the phosphorescence dies out is greater in the first process than in the second.

It will be observed that the slant of the curve, for each of the two processes, is a function of the duration of excitation.

In Fig. 40 is shown a series of curves taken under the same conditions as those of Fig. 39, except that the mercury arc was used in excitation instead of the violet end of the ordinary arc spectrum. One is immediately struck by the difference between the two sets of curves. In Fig. 40 there is a strong tendency toward parallelism in the parts of curves corresponding to the second process. In Fig. 39 no such tendency is observable.

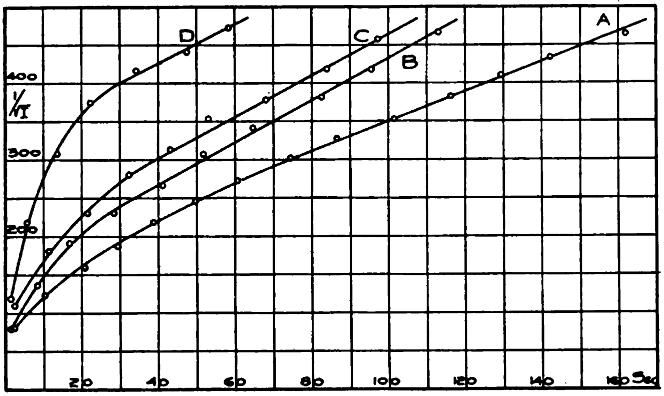

Fig. 40. Effect of duration of excitation. Violet light of mercury arc used for excitation. The curves were taken in the order indicated by the letters. The times of excitation were as follows:

Curve *A*, 27 sec. Curve *C*, 3.1 sec.
" *B*, 10 sec. " *D*, 1.2 sec.

We were at first inclined to ascribe this difference to the fact that different kinds of exciting rays had been used in the two cases. The two sets of curves differ however in another respect, namely, in the order in which the curves were taken. In the first case the curves of short excitation were taken first, while in the latter case the curves corresponding to long excitations were the first observed. It appeared possible that the difference in the form of the curves was due to this difference in sequence rather to the difference in exciting light.

To test this matter the observations plotted in Fig. 41 were made. It will be noticed that the dotted curves are similar to those in Fig. 40 while the full curves are similar to those of Fig. 39. The mercury arc was used in excitation in all cases. But curves taken after the screen had been subjected to the long excitations corresponding to Curves *C* and *D* differ widely from the curves taken with approximately the same excitation previous to *C* and *D*. A comparison of Curves *A* and *E* illustrates this point, the duration of exposure being exactly the same in each of these two cases.

These results indicate that some change is produced in the phosphorescent material by the action of the exciting light, and that this changed condition persists for a considerable period after all visible phosphorescence has ceased. In other words the effect of a given excitation in producing phosphorescence depends upon the previous history of the phosphorescent substance.

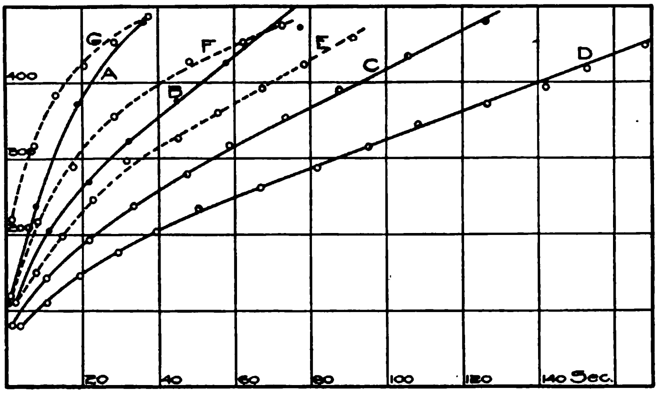

Fig. 41. Effect of duration of excitation. Mercury arc. The curves were taken in the order indicated by the letters. The times of excitation were as follows :

| | | | |
|---|---|---|---|
| Curve *A*, | 4.3 sec. | Curve *E*, | 4.3 sec. |
| " *B*, | 8.2 sec. | " *F*, | 1.4 sec. |
| " *C*, | 16.0 sec. | " *G*, | 1.0 sec. |
| " *D*, | 56.0 sec. | | |

If the screen is allowed to rest in the dark for a number of hours this semi-permanent effect of exposure in part dies out. But rest alone dose not restore the screen completely, even if continued for several days. The effect of rest was also found to be somewhat uncertain, being much greater on some occasions than on others.

Several methods of restoring the screen to a standard condition were tried. Heating the screen to the temperature of boiling water for several minutes and then cooling it again to the temperature of the room seemed effective. But this method required considerable time and has not been thoroughly tested. Cooling the screen to the temperature of liquid air and afterwards warming it gradually to the original temperature seemed to be without effect.

The well known effect of the red and infra-red rays in suppressing the long time phosphorescence of various substances led us to think that these rays might also prove effective as a means of restoring the screen to a standard condition. This conjecture proved to be correct, and exposure to the red and infra-red rays of a 50 c. p. lamp at a distance of about 20 cm. was found to be both convenient and satisfactory. A piece of ruby glass placed in front of the lamp served to remove the more refrangible rays. An exposure of a few seconds to the rays that passed through the ruby glass was sufficient to bring the screen into what seemed to be a definite standard condition. A longer exposure was, however, ordinarily used.

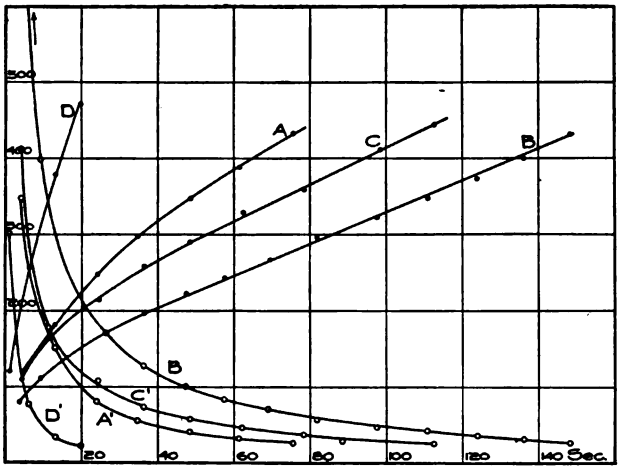

**Fig. 42.** Illustrating the relative effect of rest and of exposure to infra-red.
*A*, 10 sec. excitation after rest of 24 hours in the dark.
*B*, 2 min. excitation.
*C*, 10 sec. excitation immediately after *B*.
*D*, 10 sec. excitation after exposure of 4 min. to infra-red from 50 candle power lamp.
Curves *A′*, *B′*, *C′*, *D′* correspond to *A*, *B*, *C*, *D* except that $I$ is plotted in place $I^{-\frac{1}{2}}$.

The change produced by excitation and the effect of the red and infra-red rays are illustrated by the curves shown in Fig. 42. Curve *A* shows the behavior of the screen when exposed for ten seconds after resting in the dark for twenty-four hours. Curve *B* is that corresponding to an exposure of two minutes; Curve *C* was taken with an exposure of ten seconds immediately after Curve *B*; and Curve *D*, also with an exposure of ten seconds, was taken after the screen had been exposed to the red and infra-red rays for four minutes.[1]

In some respects the behavior of the screen is analogous to the magnetic behavior of iron. When iron is magnetized a certain residual magnetization remains after the removal of the magnetizing force, and the effect produced by a subsequent magnetizing force depends upon the magnetic history of the specimen. Similarly some change is produced in Sidot blende by excitation which does not immediately disappear upon the removal of the exciting light, and which modifies the effect produced by subsequent excitation.

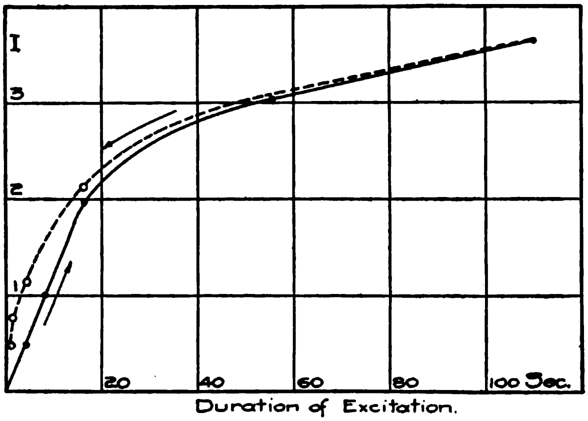

Fig. 43. Hysteresis loop. Ordinates give the intensity of phosphorescence 30 sec. after the end of excitation. The curves from which these points were determined were observed in the order indicated by the arrows.

The analogy is rendered more striking if this property of Sidot blende is exhibited in a different manner, as in Fig. 43. In the curve plotted in this figure the abscissa of each point shows the duration of excitation, while the ordinate gives the corresponding intensity of phosphorescence after thirty seconds decay. The resemblance of the curve to a hysteresis loop for iron is striking.

---

[1] Experiments dealing with the effect of the infra-red rays during and after excitation will form the subject of a separate paper.

It seems possible that the action of these rays in destroying the residual effect in the phosphorescent substance is similiar to the effect of jarring or tapping in destroying the residual magnetism of a bar of iron. Ignorance of the existence of hysteresis would evidently lead to confusing results in the case of either of these two classes of phenomena. Our delay in recognizing the effect of previous history has in fact made it necessary for us to discard all of our earlier observations.

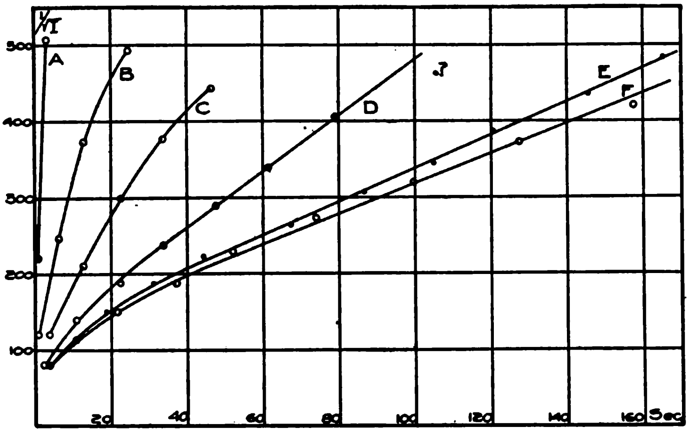

**Fig. 44.** Effect of duration of excitation. Violet of mercury arc used for excitation. Screen exposed to infra-red for 1 min. before each curve. The times of excitation were as follows:

Curve *A*, 1.2 sec.
" *B*, 5.4 sec.
" *C*, 12.0 sec.
Curve *D*, 37 sec.
" *E*, 60 sec.
" *F*, 15 min.

In our later work the screen was exposed to the red and infra-red rays as described for one minute before each exposure. With this precaution to avoid the effects of hysteresis the curves shown in Fig. 44 were taken to determine the effect of varying times of exposure.

Since our previous experiments have shown that the curves are accurately straight in the neighborhood of $t = 0$, it is possible to determine the initial intensity of phosphorescence by prolonging the curves in each case until they strike the vertical axis. From the intercept thus determined, which is equal to $I_0^{-\frac{1}{2}}$, the initial intensity can be computed. From the results obtained in this way from the data shown in Fig. 44, Curve *A* in Figs. 45 and 46 has been plotted. In these two figures *I* has been plotted instead of $I^{-\frac{1}{2}}$.

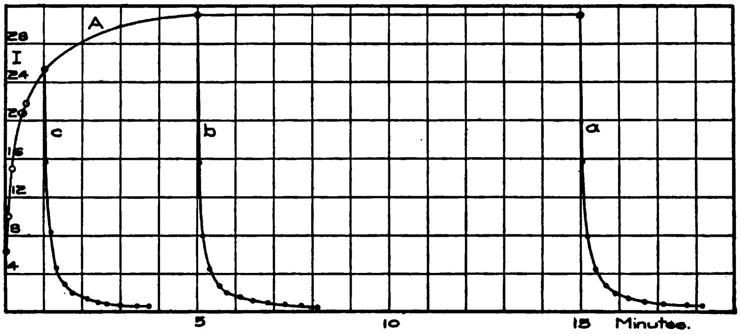

Fig. 45. Effect of duration of excitation. Curve *A* shows the initial intensity of phosphorescence (*I*) as a function of the time of excitation. Curves *a*, *b* and *c* show the decay of phosphorescence after excitations of 15 min., 5 min. and 1 min., respectively.

It will be noticed that the intensity of phosphorescence at first increases rapidly with increased duration of exposure, but that after an exposure of two or three minutes is reached there is little further change. The phosphorescence may be said to be saturated so far as the effect of duration of excitation is concerned. Not only is the initial intensity unaltered by longer excitation, but the form of the decay curve also remains constant, as is indicated by Curves *a* and *b* in Fig. 45. (These curves correspond to Curves *F* and *E* of Fig. 43.)

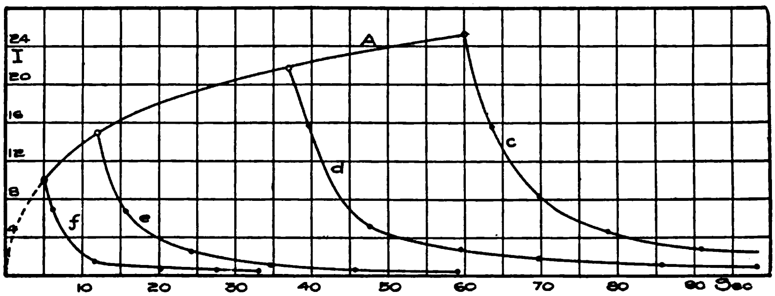

Fig. 46. Effect of duration of excitation. A portion of the same curve shown in Fig. 45 plotted to a larger scale.

We have also studied to some extent the influence of the intensity of the exciting light upon the form of the decay curves. In order to vary the intensity of the exciting light several metal stops were prepared, which could be placed immediately in front of the mercury lamp. The apertures of these varied from one millimeter in diameter to the full size of the mercury lamp tube, namely, 15 mm. To determine the intensity of the exciting light corresponding to each of these the following photometric method was used: The phosphorescent screen was removed from the photometer and a piece of white cardboard was put in its place. This being illuminated by the violet light from the mercury arc passing through the stop whose constant was to be determined, the intensity was measured by shifting the position of the comparison flame on the opposite side of the photometer. Suitable glass screens were used to equalize the colors on the two sides. To avoid errors resulting from the flickering of the mercury arc ten settings were made for each determination.

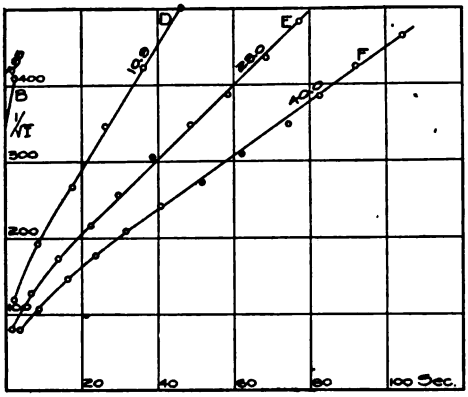

Fig. 47. Effect of varying the intensity of the exciting light. Exposure in each case 20 sec. The relative intensity of the exciting light is marked on each curve.

In Fig. 47 decay curves are shown for different intensities of the exciting light, the excitation in each case lasting for twenty seconds. In Figs. 48 and 49 similar sets of curves are shown for which the excitations were respectively 40 seconds and 2 minutes.

A study of these curves shows that there is some approach to intensity saturation; in other words, the intensity of phosphorescence is nearly proportional to the intensity of the exciting light for small values of the latter, but increases less rapidly than the excitation when the exciting light is strong. This point is well brought out by Curve *A* in Fig. 50, in which the ordinates are proportional to the initial intensity of phosphorescence, $I_0$. The values of $I_0$ were determined from the data of Figs. 47, 48 and 49 by extrapolation, upon the assumption that the relation between $t$ and $I^{-\frac{1}{2}}$ is linear for small values of $t$. Since the early portion of each decay curve is chiefly determined by the first two or three points, which are the most difficult to observe, the values plotted for $I_0$ are subject to considerable error. Curve *A* is nevertheless reasonably

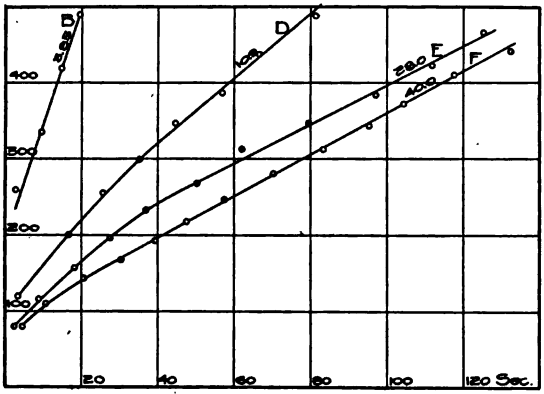

Fig. 48. Effect of varying the intensity of the exciting light (as indicated on each curve). Exposure in each case 40 sec.

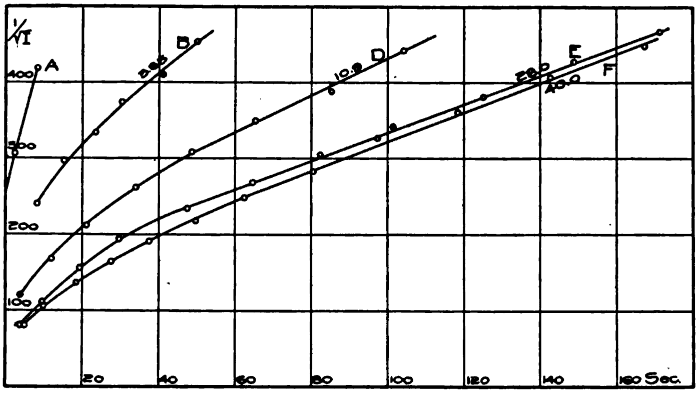

Fig. 49. Effect of varying the intensity of the exciting light (as indicated on each curve). Exposure 2 min. in each case.

smooth and indicates nearly exact proportionality between intensity of excitation and initial phosphorescence. It is only with the most intense excitation used that saturation begins.

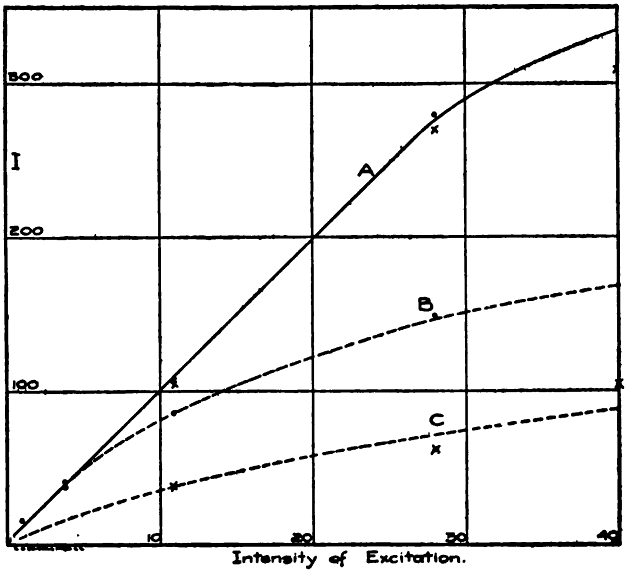

Fig. 50. Curve *A*. Effect of the intensity of the excitation upon the initial intensity of phosphorescence. The points marked by dots are for an exposure of 2 min.; those indicated by crosses are for an exposure of 20 sec. In Curves *B* and *C* the ordinates show the intensity of phosphorescence 1 min. after excitation had ceased.

It is to be observed that in most cases the values of $I_0$ that are computed from the data of Fig. 47 lie on the same curve as those obtained from the data of Fig. 49. A well-marked difference is noticeable only in the case of the points corresponding to intense excitation. In other words, for weak excitations the intensity of the initial phosphorescence is the same after an exposure of 20 seconds as for one of two minutes. There at first appears to be a contradiction here to the results shown in Figs. 45 and 46. But while this may be due to the uncertainty in the values of $I_0$, it is readily explained upon the assumption that a weak excitation produces its full effect more promptly. The form of the curves shown in Figs. 45 and 46 is probably largely dependent upon the intensity of the exciting light.

The ordinates of Curves *B* and *C* (Fig. 50) show the intensity of phosphorescence one minute after the exciting light was cut off. For Curve *B* the exposure was two minutes, while for Curve *C* the exposure was twenty seconds. The effect of duration of exposure is here well marked.

In the case of exposures lasting for several seconds or more the phenomena are manifestly complicated by the fact that the semipermanent change, to which we have already referred, is taking place in the active substance during the time of excitation. It seemed probable that the relation between intensity of excitation and intensity of phosphorescence might prove simpler if the duration of excitation was reduced to a minimum. A series of curves was therefore taken with a spark as exciting source. Preliminary trials showed that the most intense excitation was furnished by discharging eight large jars through a spark gap about 2 cm. long with one cadmium terminal. The distance of the spark gap from the screen was varied from about 10 cm. to 35 cm. A single spark at 10 cm. distance gave an excitation approximately equivalent to thirty seconds exposure to the mercury arc.

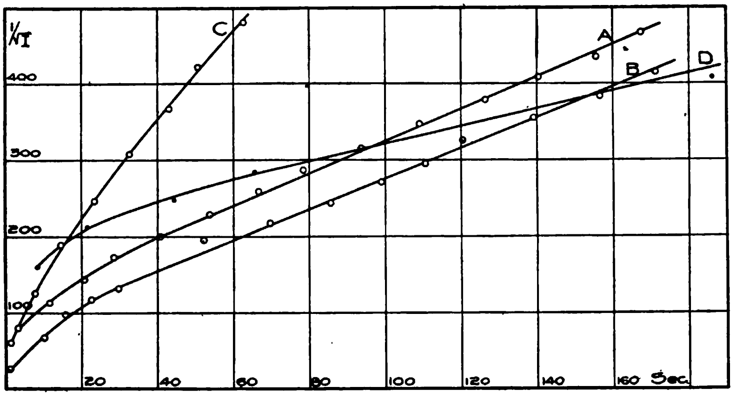

Fig. 51. Typical decay curves for various substances. Curve *A*, Sidot blende; Curve *B*, "Emanations-pulver"; Curve *C*, Willemite; Curve *D*, Balmain's paint.

Experiments with the practically instantaneous excitation produced by a single spark showed that the phosphorescence was proportional to the intensity of excitation, not merely initially but throughout the whole period of decay. In other words, it was possible to bring a decay curve determined with the spark at a distance $d_2$ into coincidence with the curve corresponding to the distance $d_1$ by multiplying each ordinate $I_2$ by the ratio $d_2^2/d_1^2$.

## EXPERIMENTS WITH DIFFERENT PHOSPHORESCENT SUBSTANCES.

It is natural to inquire whether the complex phenomena exhibited by Sidot blende are peculiar to this particular material, or whether its behavior is typical for a large class of phosphorescent substances. In order to test this matter we have determined the decay curves under similar conditions with three other substances, namely, "Emanations-pulver,"[1] willemite and Balmain's paint. Characteristic curves for these three substances together with a representative curve for Sidot blende are shown together in Fig. 51. It will be noticed that the curves are all of the same type. In each case the decay is at first rapid and apparently according to the same law that was found to hold during the early stages of decay in the case of Sidot blende. After twenty or thirty seconds the curves begin to bend, and finally become straight lines whose slant is less than that of the earlier part of the curve.

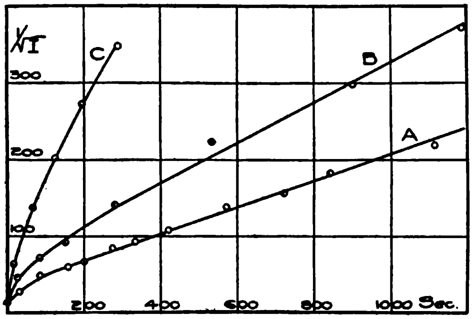

Fig. 52. Decay curves plotted from the data of E. Becquerel. (Ann. de Chimie et de Physique, series 3, Vol. 62, 1861.)

Curve *A*, Sulfure de calcium lumineux vert (2, p. 69).
" *B*, Sulfure de strontium lumineux vert (p. 71).
" *C*, Sulfure jaune-orangé vif (p. 68).

---

[1] Obtained from Leppin and Masche, who do not state the composition of the powder. It is said to be especially sensitive to the influence of the radioactive emanations.

Upon plotting the data of E. Becquerel[1] in the same manner we find that in several cases the curves are of exactly the same type as those obtained by us. Three such curves are shown in Fig. 52. In fact all the data recorded by Becquerel in his classic papers on this subject give curves which show the same general characteristics, although in several instances the curves are not so smooth as those shown in this figure.

It is interesting to note also that the data of Darwin[2] on Balmain's paint give a curve similar to those obtained by us with this substance when plotted in the same way. Two decay curves taken by E. Wiedemann[3] with Balmain's paint also show the same characteristics.

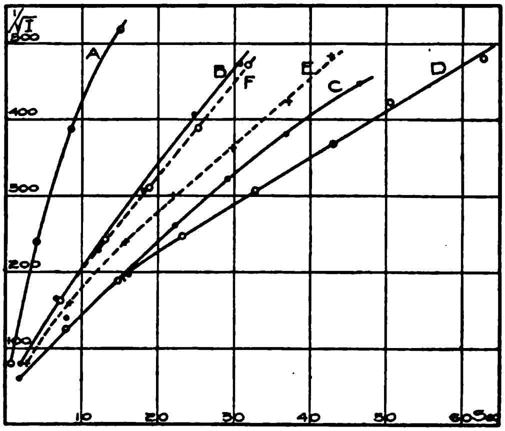

Fig. 53. Willemite. Excited by a spark between iron terminals. The curves were taken in the order indicated by the letters, and with the excitations stated below:

| | | | |
|---|---|---|---|
| Curve *A*, | 0.7 sec. | Curve *D*, | 60.0 sec. |
| " *B*, | 3.4 sec. | " *E*, | 3.9 sec. |
| " *C*, | 9.0 sec. | " *F*, | 1.0 sec. |

It appears therefore that the decay curve for Sidot blende is similar in its main features to the curves obtained for a large number of other phosphorescent substances. In fact we do not know of any case of long time phosphorescence which shows a different type of curve.

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[1] Becquerel, La Lumière. Also Annales de Chimie et de Physique, Series 3, Vol. 62, 1861.

[2] Darwin, Philosophical Magazine, Vol. 11, p. 209, 1881.

[3] E. Wiedemann, Zur Mechanik der Leuchtens, Wied. Ann., Vol. 37, p. 177 1889.

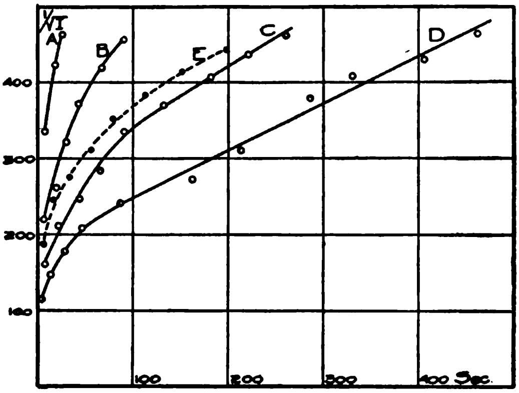

Fig. 54. Balmain's paint. The curves were taken in the order indicated by the letters, and with the following excitations:

Curve *A*, 5.9 sec.
" *B*, 12.0 sec.
" *C*, 26.0 sec.
Curve *D*, 42.0 sec.
" *E*, 6.4 sec.

The peculiar behavior of Sidot blende which we have compared with magnetic hysteresis is also exhibited by willemite and Balmain's paint, as illustrated in Figs. 53 and 54. In each of these cases it is evident that the effect of a given excitation is dependent on the previous history of the substance. We have not yet had an opportunity to test this phenomenon in other substances.

## SUMMARY.

The most important points brought out by the experiments here described may be briefly stated as follows:

1. *Form of Decay Curve.* — The curve obtained by plotting the values of $I^{-\frac{1}{2}}$ as ordinates and the corresponding values of $t$ as abscissas is a straight line for small values of $t$; it changes to a curve concave toward the axis of $t$ as $t$ increases; but for still larger values of $t$ the relation between $I^{-\frac{1}{2}}$ and $t$ is again linear, and remains so until $I$ becomes too small to measure. In other words the decay curve, when plotted in this way, consists of two straight portions which gradually merge into one another.

2. *Effect of Duration and Intensity of Excitation.* — Not only the intensity of phosphorescence, but also the form of the decay curve, is dependent on the intensity and duration of excitation. The slant is altered in each of the straight parts of the curve by changing either of these two factors in the excitation.

3. *Hysteresis.* — The behavior of the phosphorescent substance with a given excitation depends upon its previous history. Some semi-permanent change is produced by excitation which persists for several hours, or even for several days, after visible phosphorescence has ceased.

4. *Effect of Red and Infra-red Rays.* — In the case of Sidot blend the semi-permanent condition produced by excitation may be destroyed and the screen restored to a standard state by brief exposure to the red and infra-red rays. We have not yet determined whether the same effect is produced by the long waves in the case of other phosphorescent substances.

# AN INDUCTANCE AND CAPACITY BRIDGE.

By A. de Forest Palmer, Jr.

THE apparatus described herein, was developed, primarily, for the use of students in the Physical Laboratory of Brown University, the idea being to provide easily workable methods by which inductances and capacities can be compared, with an accuracy of about one tenth of one per cent., without the use of elaborate or expensive instruments. While the precision sought is considerably below that desirable in the most exact work, it is amply sufficient for the purpose and, indeed, for most practical work. With the exception of the resistance boxes, condenser and galvanometer, all of the necessary apparatus was built in the laboratory and, though somewhat roughly constructed, it gave results well within the desired limit. A brief description of its essential features is, accordingly, given in the hope that it may be found useful in other laboratories.

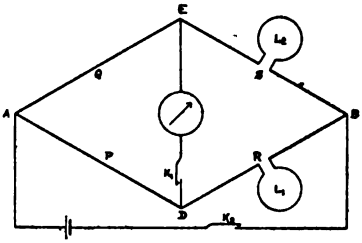

Fig. 1.

Maxwell's[1] method for the comparison of two inductances ($L_1$ and $L_2$) is illustrated in Fig. 1. $P$ and $Q$ are noninductive resistances; $R$ represents the resistance of the coil $L_1$ plus the noninductive resistance in series with it between $B$ and $D$, and $S$ bears the same relation to $B\,E$. When the bridge is in balance for alternating or intermittent currents,

$$\frac{L_1}{L_2}=\frac{P}{Q} \tag{1}$$

provided the steady current relation

$$PS=QR \tag{2}$$

---

[1] Maxwell, "A Treatise on Electricity and Magnetism," third edition, Vol. II., p. 398.

is also fulfilled. Fig. 2 shows Maxwell's[1] arrangement for the comparison of an inductance with a capacity. The letters have the same significance as in Fig. 1 with the addition of $C$ to represent the capacity of the condenser. When the resistances are so chosen that equation (2) is satisfied and the bridge is also in balance for alternating currents

$$L = CQR. \tag{3}$$

Under suitable conditions, these methods are very sensitive but, owing to the necessity of a double adjustment for direct and alternating current, their practical application is somewhat tedious. A further difficulty arises from the fact that few resistance boxes are subdivided sufficiently to permit an exact balance. If the fine adjustment is accomplished with an ordinary slide wire, the battery and galvanometer leads cannot be kept in a fixed position and near together. Furthermore, the connection wires of the bridge will include a considerable area. The error due to the inductances thus introduced would rarely exceed one tenth per cent., but it should be avoided if possible. The tedium of the methods may be considerably reduced by taking $P$ equal to $R$ and $Q$ equal to $S$ so that the bridge is always in balance for steady currents whatever the actual value of these resistances. Balance for alternating current may then be easily attained by altering $P$ and $R$ or $Q$ and $S$ by equal amounts.

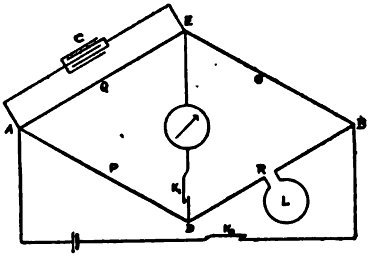

Fig. 2.

The apparatus, designed to carry out these operations and to eliminate, as far as possible, all inductances save those compared, is illustrated, diagrammatically, in Fig. 3. It is, essentially, a connection board provided with a series of brass contact blocks and three double slide wires. The blocks, taken from an old rheostat, are about 1.5 by 2 inches on the top face and .75 of an inch thick. They are bolted securely to a slab of slate and may be connected by large well fitting plugs. Each block is provided with two binding screws and a socket for the movable binding posts that terminate the battery and galvanometer leads. The slide wires $D$, $C$ and $D'$ are somewhat over one meter long and are stretched, parallel to one another, along the top of a wooden meter scale. $D$ and $D'$ are manganin, No. 22 B. S., and are soldered to small brass plates that are securely clamped to adjacent contact blocks by large binding screws. The copper wires $C$ are insulated from $D$ and $D'$, except at the sliding contacts, and may be connected to the galvanometer as indicated at $G'$. A longitudinal section of the sliders $C_1$, $C_2$ and $C_3$ is exhibited, on a somewhat enlarged scale, at $S$. These sliders are, essentially, small brass tripods with feet grooved to fit the three wires and they are held firmly in place by inverted $U$'s, of vulcanized fiber, terminating in brass springs that bear against the under side of the wooden scale. The contact pressure is transmitted and regulated by an adjusting screw that passes through the bend of the $U$ and engages the hole $H$. The resistance of these contacts was found to be very small and surprisingly constant.

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[1] Maxwell, l. c., p. 425.

Fig. 3 also shows connections arranged for the comparison of two inductances $L_1$ and $L_2$. $R_1$, $R_2$, $R_3$ and $R_4$ are variable non-inductive resistances, of the common plug cutout pattern, guaranteed, by the makers, to be accurate within one tenth per cent. The galvanometer is connected at $G$ and $G'$ and the battery at $B$ and $B'$ through a secohmmeter. In practice, equal resistances are included in $R_3$ and $R_4$, plugs are placed at 2 and 6, and balance for steady current is obtained by adjusting $R_1$, $R_2$ and $X$. After removing the plugs from 2 and 6, balance is again produced by altering $R_3$ and $Y$. Finally, with the secohmmeter in motion, balance for alternating current is attained by moving the contact $C_3$ and, if necessary, making equal changes in $R_3$ and $R_4$. Unless the resistances in the boxes at $R_3$ and $R_4$ are very well adjusted, it will generally be necessary to repeat the two latter operations but in this case, the final adjustment can always be made, with the contacts $C_2$ and $C_3$, so that exact balance is observed with either direct or alternating current.

For the comparison of an inductance with a capacity the coil $L_2$ is removed, plugs are placed at 2 and 6, the condenser is connected between $A$ and $E$, and $R_3$ is made equal to $R_4$. Balance for direct current is first obtained by altering $R_1$, $R_2$ and $X$. The adjustment with alternating current is then accomplished by making equal variations in $R_3$ and $R_4$ and moving the contact $C_3$. If necessary, these operations are repeated until the bridge is in balance for both types of current, a condition that seldom requires more than two trials.

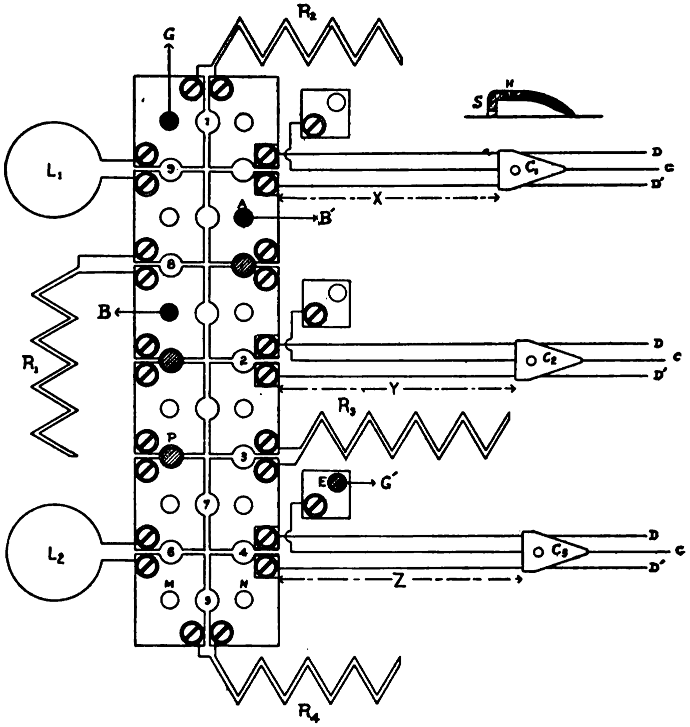

Fig. 3.

When the resistances $R_3$ and $R_4$ are so large that a variation of one ohm is within the required limit of accuracy, a plug may be placed at 4 and the condenser connected at $N$ instead of $E$.

By comparing Fig. 3 with Figs. 1 and 2, it is obvious that

$$P = R_2 + a_1 X \tag{4}$$

and

$$Q = R_3 + a_2 Y + a_3 Z, \tag{5}$$

where $X$, $Y$ and $Z$ are bridge readings; $a_1$ is the sum of the resistance per unit length of the manganin wires at $X$; $a_2$ bears the same relation to $Y$; and $a_3$ is the resistance per unit length of the wire $D$ at $Z$. Also, in virtue of the adjustments described above, $P$ equals $R$, $Q$ equals $S$, and equations (1) and (2), or (2) and (3), are satisfied.

For the purpose of testing the accuracy attainable with the apparatus, three coils ($A$, $B$ and $C$) were inter-compared by the first of the above methods and then separately compared with several different capacities by the second method. During these comparisons the sliding contacts were set to an exact balance, but readings were taken to the nearest millimeter, since the error thus introduced was always much less than one tenth of 1 per cent. of either $P$ or $Q$. Reduction of the observations was facilitated by the use of graphs, constructed with bridge readings as abscissas and corresponding resistance as ordinates. These graphs were drawn to such a scale that the products $a_1X$, etc., could read off directly with the required degree of precision. This was accomplished, on a sheet of convenient size, by drawing several parallel lines, each representing about 20 centimeters of the wire.

The results of the first series of observations are given in Tables I., II and III. $L_A$, $L_B$ and $L_C$ represent the inductance of the coils $A$, $B$ and $C$, respectively, and the other letters refer to Fig. 1. The values under $P$ and $Q$ were calculated by equations (4) and (5), and those under $L_B/L_C$, etc., by equation (1). The average deviation of a single observation from the mean is .064 per cent. in Table I., .084 per cent. in Table II., .061 per cent. in Table III.

TABLE I.

| $L_1$ | $L_2$ | $P$ | $Q$ | $L_B/L_C$ |
|---|---|---|---|---|
| $C$ | $B$ | 2.102 | 3.619 | 1.7217 |
| " | " | 3.110 | 5.361 | 1.7238 |
| " | " | 12.110 | 20.882 | 1.7244 |
| " | " | 102.083 | 175.671 | 1.7210 |
| $B$ | $C$ | 4.060 | 2.357 | 1.7226 |
| " | " | 7.056 | 4.094 | 1.7235 |
| " | " | 5.102 | 2.960 | 1.7236 |
| " | " | 6.040 | 3.500 | 1.7257 |
| | | | Mean | 1.7233 |

TABLE II.

| $L_1$ | $L_2$ | $P$ | $Q$ | $L_A/L_B$ |
|---|---|---|---|---|
| $B$ | $A$ | 7.074 | 10.025 | 1.4171 |
| " | " | 13.060 | 18.518 | 1.4179 |
| " | " | 6.105 | 8.665 | 1.4193 |
| " | " | 8.021 | 11.370 | 1.4176 |
| $A$ | $B$ | 5.081 | 3.574 | 1.4217 |
| " | " | 6.744 | 4.753 | 1.4189 |
| " | " | 9.865 | 6.952 | 1.4194 |
| " | " | 13.873 | 9.764 | 1.4209 |
| | | | Mean | 1.4191 |

TABLE III.

| $L_1$ | $L_2$ | $P$ | $Q$ | $L_A/L_C$ |
|---|---|---|---|---|
| $A$ | $C$ | 13.978 | 5.708 | 2.4489 |
| " | " | 7.860 | 3.212 | 2.4470 |
| " | " | 8.731 | 3.570 | 2.4456 |
| " | " | 24.105 | 9.842 | 2.4492 |
| $C$ | $A$ | 4.116 | 10.057 | 2.4434 |
| " | " | 8.137 | 19.897 | 2.4452 |
| " | " | 12.113 | 29.621 | 2.4454 |
| " | " | 6.120 | 14.974 | 2.4466 |
| | | | Mean | 2.4464 |

A comparison of the individual coils with the sections of a mica condenser, by Elliott Bros., is exhibited in Table IV. Column $C$ gives the nominal value of the capacities used. The sub-letters on the $P$'s and $Q$'s indicate the coil connected at $L$, Fig. 2, or $L_1$, Fig. 3, during the corresponding observation. The ratios given in the last three columns were each calculated from pairs of observations, tabulated in the same horizontal line, by the equation

$$\frac{L_A}{L_B} = \frac{P_A Q_A}{P_B Q_B}, \tag{6}$$

which follows directly from (3) when $P$ is taken equal to $R$. The average of the individual deviations from the mean is .032 per cent. of $L_A/L_C$, .049 per cent. of $L_A/L_B$, and .070 per cent. of $L_B/L_C$. Since the actual capacity of the condenser was unknown, it was impossible to determine the exact value of the inductances but an idea of their magnitude was obtained from the observations given in the first two rows of Table IV. The reduction was made by equation (3), using the nominal value of the capacity. The results were .0161 Henry for coil *A*, .0113 Henry for coil *B*, and .00658 Henry for *C*.

TABLE IV.

| $C$ | $P_C$ | $Q_C$ | $P_B$ | $Q_B$ | $P_A$ | $Q_A$ | $L_A/L_C$ | $L_A/L_B$ | $L_B/L_C$ |
|---|---|---|---|---|---|---|---|---|---|
| 1.0 | 3.132 | 2,103 | 5.092 | 2,229 | 7.062 | 2,280 | 2.4446 | 1.4186 | 1.7232 |
| 1.0 | 6.137 | 1,072 | 7.098 | 1,597 | 11.066 | 1,454 | 2.4457 | 1.4195 | 1.7230 |
| .5 | 6.139 | 2,150 | 13.094 | 1,737 | 11.066 | 2,917 | 2.4456 | 1.4193 | 1.7232 |
| .5 | 9.137 | 1,445 | 17.098 | 1,329 | 24.056 | 1,342 | 2.4452 | 1.4207 | 1.7211 |
| .2′ | 9.137 | 3,573 | 43.093 | 1,306 | 24.056 | 3,320 | 2.4464 | 1.4192 | 1.7239 |
| .2′ | 16.137 | 2,022 | 19.100 | 2,945 | 34.064 | 2,343 | 2.4460 | 1.4189 | 1.7239 |
| .2 | 16.137 | 2,040 | 19.100 | 2,971 | 34.064 | 2,365 | 2.4472 | 1.4197 | 1.7237 |
| .2 | 12.132 | 2,714 | 33.094 | 1,716 | 54.051 | 1,490 | 2.4460 | 1.4182 | 1.7249 |
| .1 | 22.132 | 2,986 | 33.100 | 3,446 | 54.067 | 2,993 | 2.4487 | 1.4187 | 1.7260 |
| .1 | 42.129 | 1,570 | 43.100 | 2,640 | 104.048 | 1,554 | 2.4447 | 1.4211 | 1.7203 |
| | | | | | | Mean | 2.4460 | 1.4194 | 1.7233 |

The observations in Table IV. may also be used, in an obvious modification of equation (3), to calculate the ratio of the capacities given in column *C*. The ratio of each of the subdivisions to the total capacity of the condenser was thus determined and the results are given in Table V. The first column gives the coil used in making the comparisons and the numbers over the other columns indicate the nominal capacity of the sections. The average deviation of a single observation from the mean does not exeeed .07 per cent. in any of these determinations.

TABLE V.

| Coil. | .5 | .2′ | .2 | .1 |
|---|---|---|---|---|
| *C* | .49902 | .20176 | .20008 | .09967 |
| " | .49830 | .20163 | .19980 | .09946 |
| *B* | .49904 | .20167 | .20002 | .09952 |
| " | .49885 | .20152 | .19960 | .09962 |
| *A* | .49880 | .20160 | .19986 | .09948 |
| " | .49850 | .20160 | .19979 | .09952 |
| Mean | .49875 | .20163 | .19986 | .09954 |

By a slight modification of the connections given in Fig. 3, the apparatus may be adapted for Anderson's[1] method of comparing inductance and capacity illustrated in Fig. 4. For this purpose, the plug at $P$, Fig. 3, is removed and a noninductive resistance $R_5$ is connected between the blocks it joined. The coil $L_2$ is removed, plugs are placed at 2 and 7, the galvanometer terminal $G'$ is removed from $E$ to $M$, and the condenser is connected between $A$ and $M$. $R_3$ is taken equal to $R_5$ and balance for steady current is obtained by adjusting $R_1$, $R_2$ and $X$. Balance for alternating current is then secured by altering $R_4$ and $Z$. After these adjustments, we have on comparing Figs. 3 and 4

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[1] Anderson, Phil. Mag., Vol. XXXI., p. 329, 1891.

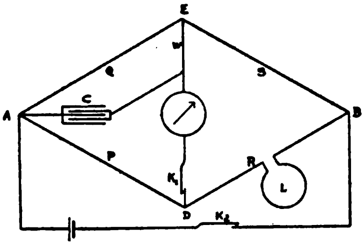

Fig. 4.

$$S = R_5 = R_3 = Q, \tag{7}$$

$$R = P = R_2 + a_1 X, \tag{8}$$

$$W = R_4 + 2a_3 Z, \tag{9}$$

where the significance of the letters is apparent from the figures and the discussion of equations (4) and (5). Hence the inductance $L$ may be determined in terms of the capacity $C$ by the well-known formula

$$L = C\{W(P + R) + PS\}, \tag{10}$$

or, since $R$ is equal to $P$, by the formula

$$L = CP(2W + S). \tag{11}$$

The foregoing examples are sufficient to show the application of the apparatus in methods depending on the principle of Wheatstone's bridge. The advantages gained by its use arise from the compact arrangement of the connections and the employment of noninductive slide wires. Provided the resistances, included in $R_1$,

$R_2$, etc., are properly constructed, the bridge is practically free from inductance except in the coils under comparison. The necessary adjustments can be rapidly and accurately made without changing the relative position of the battery or galvanometer leads. The results, quoted in the above tables, show that inductances and capacities can be compared, by the methods described, with a precision equal to that of the available resistances.

Brown University,
April 20, 1906.

# AMERICAN PHYSICAL SOCIETY.

## DIRECT READING METHODS OF RESISTANCE COMPARISON.

BY F. A. WOLFF.

THE paper contains a description of direct-reading methods employed at the Bureau of Standards for the intercomparison of resistance standards and for the calibration of resistance boxes.

The former are compared by the aid of a shunt compensated ratio set of which one arm is subdivided into four sections each provided with a ten-step shunt dial. The total resistance is thus adjustable in steps of one millionth with a range of one per cent. The principle may be applied to the Wheatstone bridge method and the Kelvin double-bridge method.

For the calibration of resistance boxes a modification of the method of Matthiessen and Hockin is employed, the bridge wire being replaced by a series of equal coils of relatively high resistance so arranged that any desired number may be put in series. By the aid of a Varley switch, any four adjacent coils may be shunted by a circuit of equal resistance including at its middle part a bridge wire corresponding to a range of ± 1 per cent. The method may be illustrated by the following example: To compare the coils of a box of a given decade, the first coil of the next higher decade and sum of the coils of the next lower decade, they are connected in series and joined in parallel with the calibrating apparatus. The number of steps required is given by the sum of the quotients obtained by dividing the nominal values of the separate coils by their greatest common divisor, thus for a series $\Sigma 1$, 1, 2, 2, 5, 10, twenty-one are required while if a standard is included twenty-two steps are necessary. Balance readings are taken for each contact block of the box and the differences between adjacent readings give the relative values of the coils intercompared. Connecting resistances in the box are eliminated by taking two readings at their terminals while the resistance of the leads to the calibrating apparatus is eliminated in the usual manner by transferring battery or galvanometer connections.

The method is applicable wherever it is possible to apply a galvanometer contact to the contact blocks between adjacent coils, so long as the balance falls within the range of the bridge wire.

The advantages of the method consist in the elimination of plug and contact resistances, in the employment of only one standard per decade, in furnishing double checks for each decade and in the relative ease and rapidity with which results are obtainable.

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THE

PHYSICAL REVIEW.

# THE VELOCITY AND RATIO *e/m* FOR THE PRIMARY AND SECONDARY RAYS OF RADIUM.

By S. J. Allen.

## Introduction.

THE reasons which led the author to investigate this subject ought first to be briefly stated. While trying to demonstrate experimentally the magnetic and electrostatic deviation of the $\beta$-rays from radium, by means of the electrical method, I was surprised to find that no appreciable electrostatic deflection could be obtained by the methods at first used, and that moreover the magnetic deflection observed was much less than we would be led to expect from the results of other experimenters. Considering the great importance of this subject, affording as it does the only method we have for testing the behavior of the electron at speeds approaching that of light, it was deemed advisable to make a thorough investigation, and to find out, if possible, wherein lay the difficulties, and the non-success of the early experiments.

Before describing my own experiments it will be of interest to give a brief resumé of the work done by previous investigators on this subject, and the conclusions reached by them. Becquerel[1] was the first to state that the $\beta$-rays from radium were deflected in an electrostatic field; and by measuring this deflection, and knowing from earlier experiments the deflection of the same rays in a magnetic field, he was able to calculate their velocity, and the ratio

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[1] C. R., 130, 1900.

$e/m$, $e$ being the charge in electrostatic C.G.S. units, and $m$ the mass expressed in grammes.

His experimental method might be briefly described as follows: A pencil of $\beta$-rays was allowed to pass upward between two parallel brass plates, and to fall upon a photographic film, placed horizontally above them. The plates were insulated from one another, and maintained at a high difference of potential by means of an electrostatic machine. A thin sheet of mica was placed vertically in the path of the rays, so as to cut it into two halves. The image on the photographic film would thus be divided into two parts by a fine line in the center. If now on the application of an electrostatic field the rays are bent, then there ought to appear on the image a shadow, the width of which would correspond to the least deviable ray.

Becquerel observed such a shadow, and measuring the width of it, and knowing from other experiments the value of the magnetic deflection, he calculated the velocity of the $\beta$-particle to be about $1.6 \times 10^{10}$ cm. per sec., and the ratio $e/m$ as $1 \times 10^7$. This experiment of Becquerel was made in air at atmospheric pressure, and for this reason no very accurate estimate of the true electric field between the plates could be made, since the ionization caused by the $\beta$-rays would to a great extent disturb the potential gradient. The results of Becquerel can therefore be only considered as approximate.

The method used by Kaufmann[1] to obtain the velocities of the $\beta$-rays was entirely different, and was based on the principle of crossed spectra. The heterogeneous pencil of rays from a small speck of radium passed upward between two brass plates, through a small hole in a metal diaphragm, placed horizontally above the plates, and then fell normally upon a photographic plate, wrapped in a thin envelope of aluminium. The brass plates were insulated from one another and could be kept charged to a high difference of potential by means of a battery of small lead accumulators. The whole apparatus was enclosed inside a glass vessel from which the air could be exhausted. A magnetic field was applied parallel to the electrostatic and an exposure given for a certain time; the direction of the electrostatic field was then reversed, and a further exposure of the same time as before given, the direction of the magnetic field being the same in both cases. When the plate was developed there appeared on it two curved lines, showing that the $\beta$-particles had been deflected by both the magnetic and electrostatic fields. By measuring the deflections observed, the value of the velocity, and $e/m$ for each ray could be calculated. He found that the velocities varied from $2.36 \times 10^{10}$ to $2.85 \times 10^{10}$, and the value of $e/m$ from $1.31 \times 10^7$ to $.63 \times 10^7$. Assuming that the charge is constant, these results showed that the mass of the electron apparently increased as the velocity of light was approached.

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[1] Nachr. d. Ges. d. Weis. m. Gott., 1901.

A theory has been developed by Thomson and elaborated by Heaviside, Abraham and others, whereby the mass of the electron is considered as entirely electrical in its nature, and increases with the speed of the electron, reaching at the velocity of light an infinite value. The late values of $e/m$ obtained by Kaufmann agreed very well with those as calculated from the formulæ of Abraham. I shall discuss these results later on in this paper.

## Electrical Experiments.

The electrical method, whenever practical, is in some respects to be preferred to the photographic, in as much as many readings can be made and confirmed in the same time that it takes to make a single exposure by the latter. In my first experiments a sensitive Dolezalek electrometer was used, but it was found almost impossible to shield this and the connecting wires from electrostatic influences sufficiently to obtain accurate readings. It was therefore replaced by a sensitive gold leaf electroscope, which could be shielded very easily from the effects of the high potentials used.

*Experiment I.* — The first experiment was tried in air at atmospheric pressure, and the general arrangement is shown sketched in Fig. 1. Two zinc plates 18 cm. long were attached to insulating uprights *A* and *B*, which kept them in a vertical position about 9 mm. apart. At the bottom of the plates was placed a block of lead containing some radium bromide, covered with a thin sheet of mica, which allowed the $\beta$-rays to pass through without much absorption. The radium was so arranged that its extreme edge was in a vertical line with the plate *b*, thus causing the rays to graze the plate *b*, but allowing them to fall full upon the plate *a*.

Over the top of the plates was suspended the electroscope, the details of which are shown in the figure. The rod *c* carrying the gold leaf was insulated from the case by means of a bead of sulphur *e*. The system was charged to a potential of a few hundred volts by means of the rod *f*, which could be turned so as to touch the rod holding the gold leaf. At other times it was connected to the case, which was earthed. The bottom of the electroscope had a thin aluminum window through which the rays could pass. The time which the gold leaf took to fall through a fixed distance on the cross hair of the telescope was taken as a measure of the ionization. Part of this ionization was due to the $\beta$- and secondary rays, and part to the $\gamma$-radiations, and these could be distinguished from one another by absorption tests. Of the total about 60 per cent. was due to the $\gamma$-, and the remainder to $\beta$- and secondary rays.

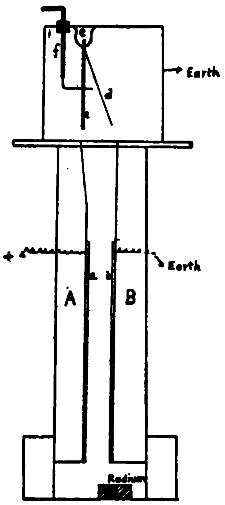

Fig. 1.

If now the plate *a* is charged positively, then the $\beta$-rays should be deflected away from the plate *b*, and a decrease of the ionization observed. This decrease would be a measure of the deflection of the rays since no fresh rays could be bent in to take the place of those bent away. If the rays travel at different velocities, then this deflection would be only an average value, but by absorbing the ones of lower velocity one ought to be able to obtain the deflection of the high velocity rays very approximately.

The plates were maintained at a difference of potential by connecting them to a battery of small lead accumulators, from which a maximum potential of 5,000 volts could be obtained. In the later experiments the number of cells was increased, so that a potential difference of about 9,000 volts was available.

When a difference of potential of 5,000 was applied to the plates no appreciable decrease of the ionization in the electroscope could be observed. The rays were completely deflected by means of a magnetic field, but the value of $HR$, $H$ being the strength of the magnetic field and $r$ the radius of curvature of the deflected rays, as calculated from this deflection was over five times what it should have been calculated from theory.

The expression for the deflection of the ray in a uniform electrostatic field is:

$$\delta = \frac{Xed\left(\frac{d}{2} + h\right)}{mV^2},$$

where $\delta$ represents the deflection, $d$ the distance travelled by the ray in the field, $h$ the distance from the top of the plates to the electroscope, $e/m$ the ratio of charge to mass of the electron, $X$ the strength of the electric field, and $V$ the velocity of the electron. In this experiment $d = 18$ cm., $h = 7$ cm. and $K = 5 \times 10^{11}$ e.m. units.

If we assume for $V$, and $e/m$, the extreme values found by Kaufmann, viz., $2.83 \times 10^{10}$ cm. per sec., and $.63 \times 10^{7}$, the calculated value of the electrostatic deflection for the highest velocity rays amounts to about 11 mm., which should have been observed since the width of the window of the electroscope was only 15 mm.

This failure to observe the electrostatic deflection could not at first be satisfactorily explained, and it was only after a number of experiments by different methods were made that the true explanation was reached. I shall discuss this point later on.

In this experiment, as in all others made in air at atmospheric pressure, we have no very definite knowledge of the uniformity of the electric field between the plates, and for this reason all the remaining experiments were carried out in a vacuum. In this case the plates can be placed closer together, and a much higher potential applied between the $m$ without a discharge taking place, the field between the plates being practically uniform.

*Experiment II.* — In Fig. 2 is sketched the general arrangement of this experiment. Two zinc plates, $a$ and $b$, 6 cm. long are insulated from one another, and kept a distance apart of 2.9 mm. by means of ebonite side pieces. Beneath the plates are fastened two ebonite blocks, forming between them a slit of about 1 mm. width, through which pass the rays from the radium contained in a capsule placed below. The capsule is covered with a thin sheet of mica, and sealed so that no emanation from the radium can escape into the surrounding vessel.

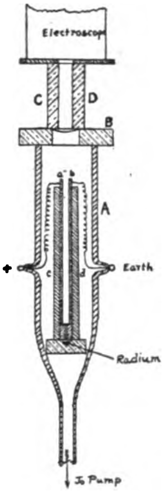

Fig. 2.

This apparatus was then enclosed in a glass vessel *A* from which the air could be exhausted to a high vacuum. The top of the vessel was closed by means of a brass cap *B*, which had an opening cut through it, and covered with a very thin sheet of zinc. Two wires sealed through the glass were connected to the two plates, and served to charge them to any desired potential difference.

On top of the brass cap were placed two parallel brass blocks, 3 cm. long and at a distance apart of 1 cm., which supported the electroscope.

The rays from the radium passed upward in a diverging beam, through the thin sheet of zinc, and into the electroscope. When the vessel was exhausted to a high vacuum the plates maintained a potential difference of 5,000 volts without a discharge; in this case we can assume that the electric field between the plates is uniform. When this voltage, which corresponds to an electric field of about reach the electroscope will consist in a large part of those of medium 10–15 per cent. in the ionization due to β-rays. The rays which 17,000 volts per cm., was applied there was a decrease of about and high velocities, since the low velocity rays are mostly absorbed in the zinc plate. If we calculate as before the deflection which might be looked for we find it to be about 8.2 mm. for the highest velocity rays, and since the distance between the plates at the electroscope is only 10 mm. this would amount to over 80 per cent. complete deflection. Those rays of lower velocity would be completely deflected. When the apparatus was placed in a magnetic field the rays could be completely deflected, though the apparent value of *HR* obtained was over three times what might be looked for.

There was a slight possibility that some of the emanation might have escaped into the vessel, in which case the true effect would be to some extent masked by the rays coming from the emanation. In order to prevent this possibility another arrangement was devised where the radium was kept entirely outside the vessel containing the charged plates.

*Experiment III.*—The experimental arrangement is shown in Fig. 3. A series of zinc plates, *a*, *a*, *a*, etc., 18 in number, were arranged parallel to one another, being insulated and kept apart by means of ebonite side strips. This arrangement was enclosed inside a glass vessel *A*, which had the walls blown out in thin bulbs immediately above and below the system of parallel plates. Alternate plates were connected together and to one electrode, the remaining plates being joined to the other electrode. The length of the plates was 4 cm., and the distance apart 1 mm. The radium was placed beneath the plates, and the electroscope above. By this arrangement a much greater amount of β-rays could get into the electroscope than in the previous experiments, and also a large electric field could be produced between the plates. A small deflection of the rays should be readily detected in the electroscope. The radium was placed about 4 cm. from the bottom of the plates, so that the increase due to rays being bent so as to enter the electroscope could not be great enough to offset the decrease due to rays bent away and absorbed.

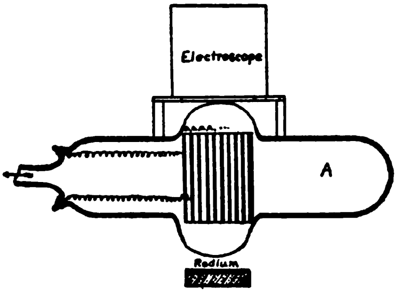

Fig. 3.

When a difference of potential of 5,000 volts was applied to the plates no very appreciable deflection could be observed. The magnetic deflection was also considerably less than one might expect from theory. The total thickness of the glass walls would have about the same absorbing power as the sheet of zinc in the previous experiment.

The results of these experiments were at first very perplexing, and no very satisfactory explanation could be reached. One was loath to conclude that the β-rays were not deviable in an electrostatic field, since Kaufmann in his carefully carried out experiments obtained results which were in such extremely good agreement with theory. Besides, the disagreement of the magnetic results with those obtained by other experimenters, seemed to show that there were present some phenomena which were affecting both alike. Nothing has been said thus far in these experiments concerning the effect of the secondary rays which are produced when the $\beta$- and $\gamma$-rays strike upon various substances. This effect was from the first considered, and was thought to be too small to account for the results obtained, but, after some further experiments, the conclusion was reached that it played in all the experiments a large rôle and in some cases the principal one.

When the $\beta$-rays, cut down to a narrow pencil by means of slits, were allowed to pass through an opening in the bottom of the electroscope considerably wider than the supposed width of the pencil, it was found, on placing a narrow strip of lead over the opening in different positions to cut off only a portion of the opening at one time, that the decrease in ionization was the same for any part of the opening. This showed clearly that the rays coming through the opening were not confined to a narrow pencil, as supposed, but spread out into a diffuse, uniformly distributed beam.

A photographic plate placed over the opening showed on development a broad, uniformly dense image, instead of the sharp narrow one, which ought to be made by the $\beta$-rays alone. This broadening of the pencil of the rays is unquestionably caused by the secondary radiation produced by the primary $\beta$- and $\gamma$-rays. If this secondary radiation was of the nature of $\gamma$-rays, then it would not be deflectable in a magnetic or electrostatic field, and could consequently not affect the deflection of the $\beta$-rays, but if, on the other hand, it was of the nature of the primary $\beta$-rays, and therefore deflectable, great confusion would arise from the different radiations.

The secondary radiation produced by $\beta$- and $\gamma$-rays of radium has been the subject of investigation by McClelland,[1] Eve[2] and Kucera,[3] who found that in general it is of several kinds, both deflectable and non-deflectable in a magnetic field, and of different penetrating power. No definite knowledge was obtained of the velocities of the deflectable kind, and to this purpose the author decided to make a complete investigation of the secondary rays. Before giving an account of this investigation I would like to describe two experiments on the $\beta$-rays made by the photographic method.

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[1] Phil. Mag., February, 1905.

[2] Phil. Mag., December, 1904.

[3] Annalen der Physik, 1906.

## PHOTOGRAPHIC EXPERIMENTS.

*Experiment I.* — The arrangement used in this is essentially the same as that used by Becquerel[1] and is shown sketched in Fig. 4. Two metal plates *a* and *b* 4.2 cm. in length were placed parallel to one another in a vertical position 6 mm. apart, and insulated by means of ebonite. About 2 cm. below the plates was placed the radium, contained in a narrow crevasse in a block of lead. In the center of the radium, and midway between the plates was fastened a sheet of mica *c*, which extended from the radium up to the photographic plate *e*. This plate was wrapped in a sheet of black paper, and then placed inside a light tight box containing a thin aluminium window, through which the rays could pass without much absorption. The distance between the top of the metal plates and the photographic plate was 2.4 cm.

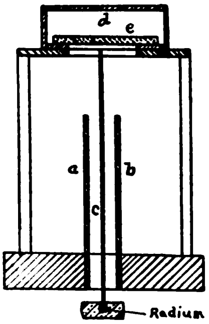

Fig. 4.

When the plates *a* and *b* are uncharged there ought to be obtained on the photographic plate an image crossed in the center by a narrow band. On the other hand when the plates are charged to a high potential if the rays are deflected to one side, the photographic plate should show a broad shadow cast by the mica screen. In *A* and *B*, Fig. 5, are shown two photographs obtained by this method, *A* taken without an electric field, and *B* with a potential difference between the plates of 3,000 volts, corresponding to a field strength of 6,000 volts per cm. Both photographs appear precisely alike and show no indication of any shadow on the plate. One side in both photographs appears darker than the other; this is on account of the mica screen not being placed exactly in the middle of the radium, thus throwing more rays to one side than to the other. In *C* and *D* are shown two photographs taken with the screen placed exactly in the center, *C* being without a field and *D* with one; and both sides of the image now appear equally dense. These photographs were all taken with the radium covered with a thin sheet of mica, so that no emanation could escape and affect the plate. Experiments were also tried with the radium uncovered, and the same results were obtained as before. Radium when dry and at ordinary temperatures does not give off very much emanation.

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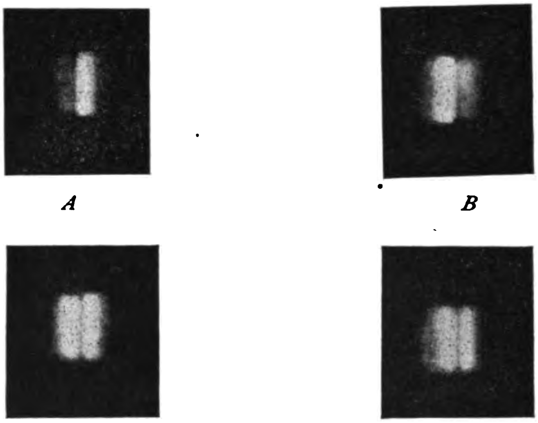
[1] Loc. cit.



*A* *B*

*C* *D*

Fig. 5.

*Experiment II.* — The arrangement used in this experiment, and illustrated in Fig. 6, is essentially the same as that used by Kaufmann[1] in his work. Two brass plates, *a* and *b*, placed parallel to one another inside a brass box *A*, were insulated from the sides by means of ebonite bushings *c* and *d*. Beneath the plates was fastened a small speck of radium bromide, and above the plates a thick ebonite screen, which had a hole 0.5 mm. cut in it through which the rays could pass in a narrow pencil. At the top of the brass box was placed a photographic plate wrapped in a sheet of black paper. The whole apparatus was enclosed inside a glass vessel which could be exhausted to a high vacuum.

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[1] Loc. cit.

Exposures of one, two and four days were made, with and without an electric field, but in no case could any sharp image due to β-rays be obtained on the plate, the only effect being a darkening of the whole plate due to γ- and secondary radiations. When the radium was left uncovered the darkening of the whole plate was much greater, due to the emanation diffused throughout the vessel.

In another arrangement a larger quantity of radium contained in a lead capsule was placed outside the brass box, and the rays allowed to enter through a small hole, and thence through an ebonite diaphragm placed just beneath the brass plates *a* and *b*.

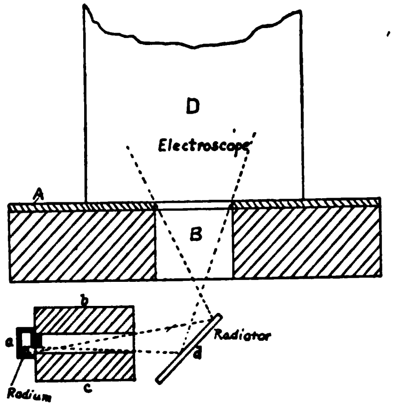

Fig. 6.

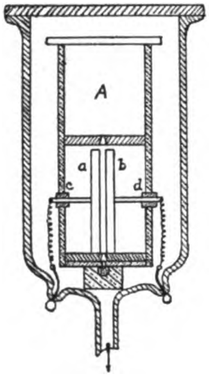

Fig. 7.

This failed to give any better results than before; and all further attempts to repeat Kaufmann's experiment were then abandoned. Probably with better photographic skill in restraining the darkening effect due to γ- and secondary rays I might have succeeded in obtaining a clear image of the β-rays. The radium used in this experiment was some kindly loaned me as that used by Kaufmann in his last experiments, if not stronger.

## Secondary Radiation.

The experimental arrangement used to study the secondary radiation is shown diagramatically in Fig. 7. About 300 milligrammes of radium bromide of about 30,000 activity was sealed in a very thin glass tube of 1.5 mm. diameter and about 5 cm. long. This tube was enclosed inside a lead box *a*, which had a slit 5 cm. long and 1 mm. wide cut in one side, the walls of the lead box being of such a thickness that no $\beta$-rays could pass through. This box was cemented to two thick ebonite blocks *b* and *c* in such a manner, that one edge of the slit coincided with a face of one of the blocks as indicated in the figure. A divergent beam of $\beta$-rays thus emerged from the slit and was limited in width by the walls of the ebonite blocks. This apparatus was placed so that the rays traveled in a horizontal direction.

Directly above and parallel to the ebonite blocks was supported a thick screen *A*, constructed of cardboard and filled with mercury, and having in the center a wide rectangular opening through which the radiations could pass into a gold-leaf electroscope placed above. The substances which were to be studied as sources of secondary radiation were placed beneath this opening in such a position that the $\beta$-rays fell full upon them. The thick mercury screen absorbed a large part of the $\gamma$-radiation; and although it introduced a small amount of secondary radiation, this increase was more than offset by the decrease of the $\gamma$-rays. The ionization in the electroscope, due to the secondary radiation from below, would under these conditions form a much larger proportion of the whole than when the full $\gamma$-rays were present.

When the radiator *d* is not present, the ionization in the electroscope is due to $\gamma$-rays and to secondary rays produced by them.

When the radiator is placed in position this ionization will be increased by that due to the secondary rays from below. By fixing radiators of different materials in the position *d*, and placing screens of varying absorbing power under the opening *b*, a knowledge of the relative penetrating power of the secondary radiations from the different radiators can be obtained. When a thick screen is placed so as to cut off the $\beta$-rays, then the increase of ionization will be due to the secondary rays caused by the $\gamma$-rays striking the radiator *d*.

In Table I. are shown a characteristic series of readings for different radiators, under various conditions.

## Table I.

*Radiator—Air and Surrounding Objects.*

| Total Rate of Leak. | Rate of Leak Due to Secondary Rays. | Absorbing Material. | Per Cent. Unabsorbed Rays. | Remarks. |
|---|---|---|---|---|
| 3.61 | 1.01 | 0 | 100 | No radiator at *d*. |
| 3.02 | .42 | 4 sheets paper | 41 | Paper placed on top of mercury screen. |
| 2.94 | .34 | 8 " " | 34 | |
| 2.85 | .25 | 16 " " | 25 | |
| 2.70 | .10 | 34 " " | 10 | |
| 3.28 | .68 | 50 " " | | Paper placed below screen placed over β-rays. |
| 3.29 | .69 | | | |

*Radiator—Zinc.*

| Total Rate of Leak. | Rate of Leak Due to Secondary Rays. | Absorbing Material. | Per Cent. Unabsorbed Rays. | Remarks. |
|---|---|---|---|---|
| 10.20 | 7.10 | 0 paper | 100 | In this set of readings the absorbing layers of paper were placed directly over radiator *d*. |
| 8.85 | 5.75 | 2 " | 81 | |
| 7.76 | 4.66 | 4 " | 66 | |
| 6.21 | 3.11 | 8 " | 44 | |
| 4.74 | 1.64 | 16 " | 23 | |
| 4.09 | .99 | 24 " | 14 | |
| 3.53 | .43 | 40 " | 6 | |
| 3.28 | .18 | 60 " | 2.5 | |

*Radiator—Zinc.*

| Total Rate of Leak. | Rate of Leak Due to Secondary Rays. | Absorbing Material. | Per Cent. Unabsorbed Rays. | Remarks. |
|---|---|---|---|---|
| 5.00 | 1.90 | 0 paper | 100 | β-rays partly screened by 24 sheets of paper. |
| 4.51 | 1.41 | 4 " | 74 | |
| 4.18 | 1.08 | 8 " | 57 | |
| 3.80 | .70 | 16 " | 37 | |
| 3.82 | .72 | 0 " | 100 | β-rays screened by piece of zinc. |
| 3.59 | .49 | 20 " | 68 | |
| 3.42 | .32 | 36 " | 44 | |
| 3.31 | .21 | 86 " | 29 | |

| Total Rate of Leak. | Corrected Leak. | Absorbing Material. | Per Cent. Unabsorbed Rays. | Remarks. |
|---|---|---|---|---|
| 3.82 | .72 | 0 | 100 | Zinc screen over β-rays. |
| 3.30 | .20 | 0 | 100 | 2 zinc screens over β-rays. |
| 3.24 | .14 | 100 | 70 | 2 zinc screens over β-rays. |
| *Air,* 3.10 | .00 | 0 | 0 | Radiator removed. |

*Radiator—4 Sheets of Paper.*

| Total Rate of Leak. | Corrected Leak. | Absorbing Material. | Per Cent. Unabsorbed Rays. | Remarks. |
|---|---|---|---|---|
| 4.96 | 1.86 | 0 | 100 | |
| 4.18 | 1.08 | 4 | 58 | |
| 3.69 | .59 | 8 | 31 | |
| 3.34 | .24 | 10 | 13 | |
| 3.21 | .11 | 32 | 6 | |

*Radiator—8 Sheets of Paper.*

| | | | |
|---|---|---|---|
| 5.29 | 2.19 | 0 | 100 |

*Radiator—16 Sheets of Paper.*

| | | | |
|---|---|---|---|
| 5.81 | 2.71 | 0 | 100 |

*Radiator—28 Sheets of Paper.*

| | | | |
|---|---|---|---|
| 6.45 | 3.35 | 0 | 100 |
| 4.80 | 1.70 | 4 | 51 |
| 4.13 | 1.03 | 8 | 31 |
| 3.57 | .47 | 16 | 14 |
| 3.29 | .19 | 32 | 6 |
| 3.23 | .13 | 82 | 4 |

*Radiator—Glass.*

| | | | |
|---|---|---|---|
| 7.52 | 4.42 | 0 | 100 |
| 4.86 | 1.76 | 8 | 39 |

*Radiator—Lead.*

| | | | |
|---|---|---|---|
| 11.36 | 8.26 | 0 | 100 |
| 6.85 | 3.75 | 8 | 45 |

*Radiator—Copper.*

| Total Rate of Leak. | Corrected Leak. | Absorbing Material. | Per Cent. Unabsorbed Rays. |
|---|---|---|---|
| 8.88 | 5.68 | 0 | 100 |

*Radiator—Iron.*

| | | | |
|---|---|---|---|
| 8.69 | 5.59 | 0 | 100 |
| 5.34 | 2.24 | 8 | 40 |

From a study of these results we see at once that substances when struck by $\beta$-rays give out secondary rays which differ amongst themselves both in quantity and penetrating power.

In order to produce the maximum amount of secondary rays the substance has to be of sufficient thickness to completely absorb all the $\beta$-rays which fall upon it. The amount of secondary radiation due to the $\gamma$-rays is only a very small quantity of the total, provided the thickness of the radiator is only just sufficient to absorb all the $\beta$-rays. When only the most penetrating $\beta$-rays are allowed to fall upon the radiator, the secondary radiations produced are on an average of a much more penetrating nature, than when all the $\beta$-rays are present. This is partly due to the fact that the secondary rays due to the high velocity $\beta$-rays are more penetrating, and also partly to the presence of a small amount of secondary $\gamma$-rays caused by the primary rays. The denser a substance is, the greater will be the amount of the secondary rays produced, and the greater their penetrating power. Of those substances examined, lead proved to be the most efficient, and also gave rays of the most penetrating power, while paper was the least. For the sake of comparison I give in Table II. the results of an absorption test on the primary $\beta$-rays (which of course contained a certain amount of secondary rays), together with the results obtained for the secondary radiation from zinc and paper.

## Table II.

| Layers of Paper. | Primary $\beta$-Rays. | Secondary from Zinc. | Secondary from Paper. |
|---|---|---|---|
| 0 | 100 | 100 | 100 |
| 2 | 82 | 81 | |
| 4 | 70 | 66 | 51 |
| 8 | 52 | 44 | 31 |
| 16 | 33 | 23 | 14 |
| 24 | 22 | 14 | |
| 32 | 15 | | 6 |
| 44 | 9.7 | 5.8 | |
| 60 | 5.0 | 2.5 | |

The penetrating power of the secondary rays from zinc does not differ very greatly from that of the primary $\beta$-rays, especially for the first few sheets of paper. The penetrating power of the sec-

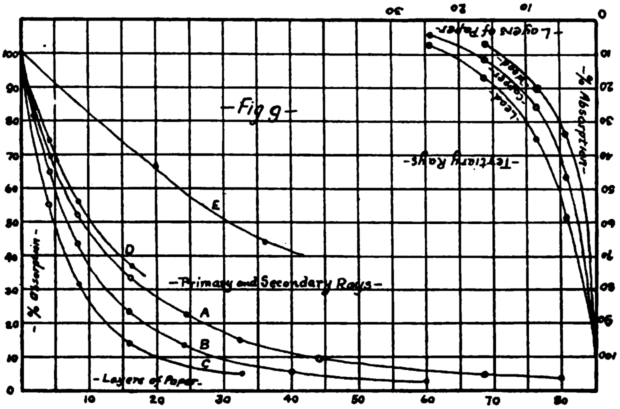

Fig. 8.

ondary rays from lead is only slightly greater than that of the rays from zinc.

In Fig. 8 are drawn several absorption curves, both for the primary $\beta$-rays, and for the secondary rays. *A* represents that for the primary $\beta$-rays, *B* that for the secondary rays from zinc, *C* that for the secondary from paper, *D* the secondary from zinc when the primary $\beta$-rays have passed through 28 sheets of paper, and *E* that for the secondary from zinc when the primary $\beta$-rays have passed through one sheet of zinc. It is seen at once from these curves that the radiations are not homogeneous, but travel at different velocities.

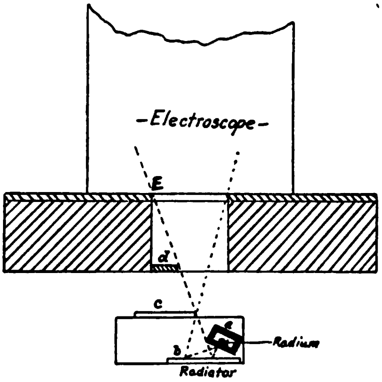

Fig. 9.

It is well known that a part of the secondary rays are deviable in a magnetic field, and in the same direction as the $\beta$-rays would be. The magnetic deflections of the secondary rays from lead, and from paper, were tried by the method illustrated in Fig. 9. The primary $\beta$-rays from the radium enclosed in the lead box *a* striking the radiator *b*, produced secondary rays which passed up into the electroscope. Screens of lead *c* and *d* were so placed that the secondary rays from the radiator could just touch the upper edge *E* of the mercury screen. Experiments were performed with both lead and paper as radiators, and in both cases it was found that the secondary

Table III.

| Field Strength. | Per Cent. Undeflected Rays. | |
|---|---|---|
| | Lead. | Paper. |
| 0 | 100 | 100 |
| 90 | 66 | 58 |
| 180 | 36 | 34 |
| 270 | 21 | 28 |
| 380 | 11 | 14 |
| 450 | 8 | 10 |

rays produced were deflected towards the right, when a magnetic field was applied in such a direction, that the lines of force can be represented as going into the plane of the paper. The results obtained in this experiment are expressed in the preceding (Table III.).

These results show that the secondary radiations from both metals and insulators consist for the most part of negatively charged particles. Those from insulators are more easily deflected than those from the more dense metals, but the difference is not very great. The proportion of non-deviable rays in the secondary rays from paper is greater than in that from zinc.

## Tertiary Rays.

When the secondary radiation strikes upon objects there is produced a third type of radiation called the tertiary rays. This radiation has been studied in the present investigation for a few substances. The method employed was precisely the same as that used for the secondary rays, with the exception that the small glass tube containing the radium, instead of being placed in front of the opening in the lead box, was moved to one side, so that no $\beta$-rays could emerge from the opening. Under these conditions the $\beta$-rays will strike the lead walls of the lead box and produce secondary rays which will travel out through the opening.

If we place a radiator in the same position as before, there will be produced in it tertiary rays, which can pass up to the electroscope, and cause an increase of ionization. The penetrating power of these rays was studied lor lead, zinc and copper radiators, and the results are expressed in the following table.

Table IV.

| Layers of Paper. | Tertiary Radiations. | | |
|---|---|---|---|
| | Lead. | Zinc. | Copper. |
| 0 | 100 | 100 | 100 |
| 4 | 59 | 46 | 47 |
| 8 | 35 | 25 | 24 |
| 16 | 17 | 10 | 11 |
| 24 | 6 | | 2.4 |

As in the case of the secondary rays, lead proves to be the most efficient radiator, and also gives out the greatest penetrating rays. The penetrating power of the tertiary rays is considerably less than that of the secondary, that for lead in the former being only slightly greater than that for paper in the latter.

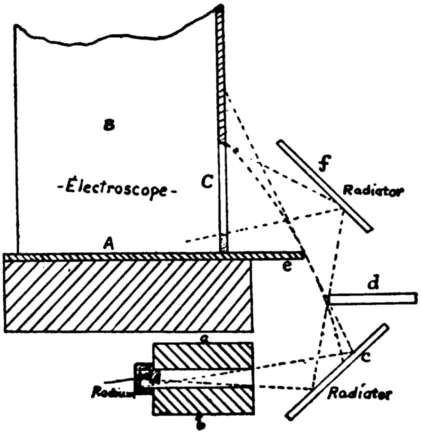

Fig. 10.

To find out whether the tertiary rays were deviable in a magnetic field, the arrangement shown diagrammatically in Fig. 10, was made use of. The mercury screen *A* was placed so that one end was directly over the ends of the ebonite blocks *a* and *b*. The electroscope *B* was placed near to the edge of the screen *A*, and had a window *c* covered with thin foil cut in one side, so that any rays might enter without absorption.

When the screen *c* was placed in position the tertiary rays produced could travel upward and enter the electroscope. Now by placing two screens, *d* and *e*, in the positions indicated in the figure, the rays could be prevented from entering the electroscope, but a portion would still be able to travel upward. When a magnetic field was applied in such a direction that the lines of force were perpendicular, and going into the plane of the paper, the ionization in the electroscope was not appreciably altered, but when applied in the reverse direction there was observed an increase in ionization. Moreover, when a screen was placed so as to cut off entirely the tertiary radiation from below, this effect was still observed but to a much less degree. These two results indicated that there was present, besides the tertiary radiation from below, a radiation which seemed to come from the mercury near the window of the electroscope. This latter radiation is undoubtedly caused by the $\gamma$-rays when they emerge from the surface of the mercury, and is the same as that observed by Eve[1] when the $\gamma$-rays were partly absorbed by a thick block of lead. By placing sheets of paper in front of the window, it was found that the penetrating power of this radiation was much less than that of the tertiary; 4 sheets of paper cut it down to 30 per cent., and 16 sheets completely absorbed it. It was also observed that when the magnetic field was increased slowly from zero, a certain strength was reached at which the increase of ionization in the electroscope due to the tertiary rays from below just became noticeable. When this happened, the rays from below were bent so that the extreme edge of the beam just entered the window. Knowing three points on the circular path of the rays the radius of curvature could at once be calculated, and was found to be about 17 cm. The strength of the magnet field was about 90 C.G.S. lines, so that we get for the tertiary rays a value of $HR = 1,530$ approximately. These results show that the tertiary rays are deviable in a magnetic field in the same direction as the $\beta$- and secondary radiation. They must therefore be negatively charged particles travelling at speeds only a little less than the slowest $\beta$-particles.

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[1] Loc. cit.

When the screen *f* is placed in the position indicated in the figure, it was found that the ionization in the electroscope was increased. This was found to be partly due to the secondary rays produced when the rays strike the screen, and also partly caused by the tertiary rays from below striking the screen, and producing a fourth type of rays.

That this latter radiation is present, can at once be shown by placing in front of the blocks *a* and *b* a screen, sufficient to cut off all the secondary rays, in which case the fourth rays are absent. This process would probably go on for a large number of radiators, but after the third the radiation is too feeble to be measured accurately. Each type of radiation is of less penetrating power than the one which produced it.

### Velocity and Ratio $e/m$ for the Primary $\beta$-Rays.

It has just been shown that the secondary $\beta$-rays have nearly the same penetrating power as the primary, and therefore, assuming for the present that they possess the same charge and mass, they must travel at velocities only slightly less. After passing through a certain thickness of absorbing material, the lower limit for both types of rays would be the same, and consequently the forward edge of a deflected beam would consist of both primary and secondary rays of the same velocity, which were just able to pass through the absorbing layer and cause ionization.

As the thickness of the absorbing layer is increased the less penetrating radiation would be more quickly absorbed, and at very thick layers, the edge of the deflected beam would consist almost entirely of the more penetrating radiation.

If, then, by any method we can find the forward edge of the deflected beam in both magnetic and electrostatic fields, we can at once calculate the velocity of those rays, both primary and secondary, which are just able to cause ionization after passing through the absorbing layer. The following method was then devised for this purpose and proved successful. It is shown illustrated in Fig. 11.

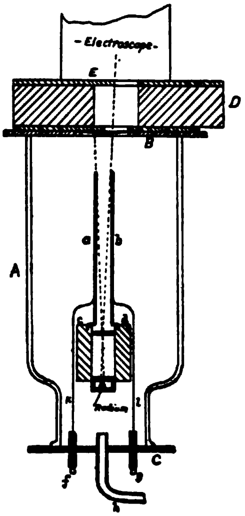

Fig. 11.

Two zinc plates, *a* and *b*, were supported in a vertical direction, and insulated from one another by means of the ebonite blocks, *c* and *d*. At the bottom of these blocks was fastened the lead box containing the glass tube of radium, and furnished with a slit 1 mm. in width, through which the rays emerged. At a short distance below the zinc plates there was placed a lead diaphragm with another slit also 1 mm. in width, which formed with the opening below a narrow pencil of rays, which travelled upward between the zinc plates. The distance between the two slits was such that the rays from the radium just touched the top edges of the plates. This apparatus was placed inside a glass vessel *A*, which was closed at the top and bottom with brass plates *B* and *C*. Through the top plate *B* there was cut a rectangular opening 1.5 cm. in width, and then covered with as thin a sheet of mica as would stand the pressure when the vessel was exhausted. The thickness of this mica window was about equivalent in absorbing power to six sheets of ordinary writing paper. The bottom plate *C* was pierced with three holes, into which glass tubes were fitted, two of them, *f* and *g*, containing the connecting wires, *K* and *L*, and the third, *H*, serving to connect the vessel to the pump.

The whole apparatus was rendered air-tight by the aid of sealing-wax; and it was found that, with an occasional stroke of the pump, the pressure could be maintained low enough to withstand a potential difference of 10,000 volts without a discharge taking place.

By connecting the wires, *K* and *L*, to the poles of the battery of lead accumulators, the zinc plates could be charged up to any desired difference of potential. In the meantime the number of the cells had been increased so that a maximum potential of 9,000 volts could be obtained.

On top of the brass plate *B* was placed the mercury screen *D*, described in the previous pages, which served to cut down in a large measure the $\gamma$-rays. The opening in this screen was partly covered at the top by a brass plate *E*, so placed that no $\beta$-primary rays could enter the electroscope. The ionization in the electroscope would then be caused by $\gamma$- and secondary rays.

The vessel was placed between the poles of a large electromagnet, of such a size that the rays during their entire course lay in a uniform field.

When the primary rays strike the sides of the slits in the lead diaphragms, secondary rays are produced which travel upward with the primary to the electroscope. The pencil of rays at the electroscope is then made up of both primary and secondary radiation, but will be prevented from entering by the brass screen *E*. This pencil of rays will, however, be confused by the presence of other secondary and tertiary rays coming from various points. This could be illustrated by some photographs taken at different points along the path of the rays. One taken 1 cm. from the upper slit shows a narrow fuzzy image; whereas at 1 mm. from the top of the zinc plates the image is sharp and the full width of the opening. At the top of the plate *B* the image had again become indistinct, while at the top of the mercury screen it was of the full width of the opening and of uniform density.

If the opening at the electroscope was arranged symmetrically with regard to the zinc plates, there was observed a decrease of ionization in the electroscope when the magnetic or electrostatic fields were applied in either direction. The decrease in the case of the electrostatic field was about 25 per cent., with a strength of field of 14,000 volts per centimeter. This shows clearly that the rays are deflectable in an electric field, though the effect observed was only about one quarter as much as might be expected.

When, however, the arrangement was the same as that described in Fig. 11, altogether different results were obtained. If the plate *a* were charged negatively, the ionization increased gradually to a maximum with increase of field, remained constant for a period, and then decreased. If, on the other hand, the plate *a* is positive the ionization decreased at once. The reason for this can be explained in the following manner.

If the plate *a* is charged negatively, the primary and secondary $\beta$-rays will be deflected to the right, and enter the electroscope, thus causing an increase of ionization.

This increase will continue until the rays have just reached the opposite side of the opening into the electroscope. When this is the case we can assume that those rays which after passing through the absorbing layer can just affect ionization, are bent the most, since all rays of lower velocity, and hence penetrating power, cannot get through the layer. The same phenomena exactly were observed when a magnetic field was applied. Consequently when the maximum point is reached for both magnetic and electrostatic deflection, the value of the velocity of the slowest ray, which can just get through the absorbing layer, can at once be calculated from the values of the electrostatic and magnetic fields. When different thicknesses of absorbing layers were placed over the opening, the strength of fields necessary to produce the maximum ionization was found to increase with increasing thickness of layer. This is what we would expect if the rays are of all different velocities, and shows, that when the maximum point is reached, the least penetrating rays for each successive layer have all been bent through the same distance.

For the sake of illustration some of these results are expressed in the accompanying table (V.).

TABLE V.

| Through 6 Sheets Paper. | | 14 Sheets Paper. | | 1.5 mm. Glass. | |
|---|---|---|---|---|---|
| P. D. | Rate of Leak. | P. D. | Rate of Leak. | P. D. | Rate of Leak. |
| 0 | 144.0 sec. | 0 | 151.0 sec. | 0 | 154.0 sec. |
| 2,700 | 134.4 " | 3,400 | 144.2 " | 4,000 | 151.0 " |
| 3,000 | 132.4 " | 3,600 | 143.4 " | 5,600 | 149.4 " |
| 3,300 | 131.6 " | 3,900 | 142.8 " | 5,800 | 148.6 " |
| 3,400 | 131.2 " | 4,100 | 141.5 " | 6,000 | 148.4 " |
| 3,560 | 131.0 " | 4,300 | 141.5 " | 6,800 | 148.6 " |
| 3,800 | 130.8 " | 6,000 | 141.4 " | | |
| 5,000 | 130.6 " | | | | |
| 6,000 | 130.6 " | | | | |
| Max. 3,500 volts. | | 4,100 volts. | | 6,000 volts. | |

In this method we do not know how far each ray is bent, since we do not know its first position, and therefore cannot obtain values of $mv/\varepsilon$, and $mv^2/e$, but, since the deflection is small compared to the length of the path, we can assume without any great error, that, for a maximum, this is the same for both magnetic and electric deflection. By comparing the electric and magnetic forces on the particle we can at once estimate its velocity. If $d$ is the distance travelled by the ray in the uniform magnetic field $H$, $l$ the length of the zinc plates, $h$ the distance from top of plates to electroscope, $X$ the strength of electric field, the velocity $V$ is given by

$$V = \frac{2Xl\left(\frac{l}{2} + h\right)}{Hd^2}.$$

In this experiment, $d = 17.0$ cm., $l = 8.4$ cm., $h = 5.5$ cm., and the distance apart of the charged plates was 6.2 mm., therefore,

$$V = \frac{2X \times 8.4\left(\frac{8.4}{2} + 5.5\right)}{17 \times 17 \times H} = \frac{0.563X}{H}.$$

As an example take the results for an absorbing layer of six sheets of paper; here $X = 3{,}500/0.62 = 5.7 \times 10^{11}$ C.G.S. units and $H = 13.5$ C.G.S. lines, and therefore we obtain,

$$V = \frac{0.563 \times 5.7 \times 10^{11}}{13.5} = 2.37 \times 10^{10} \text{ cm./sec.}$$

In order to obtain values for $e/m$, it is necessary to know either $mV/e$, or $mV^2/e$, for the different rays. Values of $mV/e$ were obtained by the following method.

The lead-box containing the radium tube was fastened to the ebonite blocks as before, but the distance between these narrowed to 2 mm., and the upper lead diaphragm removed. This arrangement allowed a broader pencil of rays than in the previous experiment to pass upward to the electroscope. Two zinc plates 3 cm. in height were fastened to the ebonite blocks in a vertical direction and so arranged that one edge of the pencil of rays could just touch the top of one of the plates. The effect of this upper plate was then to define sharply a pencil of both primary and secondary rays. This arrangement was then surrounded by a magnetic screen of soft sheet iron, which extended up to the top of the zinc plates, and kept the rays during their passage between the plates from the action of the magnetic field. The glass vessel was dispensed with and the experiment performed at atmospheric pressure, sheets of paper equivalent in absorptive power to the mica window of the previous experiment being interposed in the path of the rays. The opening at the electroscope, 1 cm. in width, was arranged as in the other experiment so that no rays of this pencil could enter the electroscope.

When a magnetic field was applied in the proper direction the ionization in the electroscope gradually increased to a maximum as the strength of the field was increased. Since the rays are only under the action of the magnetic field during their passage from the top of the zinc plates to the electroscope we can assume that, when the maximum point is reached, the least penetrating rays have been deflected over the distance represented by the width of the opening. By placing in the path of the rays suitable thicknesses of absorbing material the value of $mV/\epsilon$ for the same rays as were observed in the previous experiment could be ascertained.

These values were calculated from the following formula:[1]

$$\frac{mV}{e} = \frac{1}{2\delta}\int dx \cdot \int H dx,$$

where $\delta$ is the distance through which the rays are bent, and $H$ the value of the magnetic field at different points along the path $x$ of the rays. The value of $mV/e$ obtained by this method was $1.57 \times 10^3$ for no absorber, whereas, for 1.2 mm. of zinc it was $5 \times 10^3$; for 6 sheets of paper corresponding to the mica window the value was $1.87 \times 10^3$.

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[1] See J. J. Thomson's Discharge of Electricity through Gases, page 92.

In the former experiment in the uniform field the value of

$$\frac{mV}{e} = \frac{Hd^2}{2\delta},$$

and substituting the value of $mV/e$ obtained above, we get for the distance through which the rays were bent 1.04 cm. Knowing this value of $\delta$, all the remaining values can at once be calculated, and the complete results are shown in the following table (VI.).

TABLE VI.

| Absorbing Layer. | $X_{(\text{max.})}$ | $H_{(\text{max.})}$ | $mV^2/e$ | $mV/e$ | $V$ cm./sec. | $e/m$ |
|---|---|---|---|---|---|---|
| 0 | | | | $1.57 \times 10^3$ | 2.20 (est.) | 1.40 |
| 6 of paper. | $5.7 \times 10^{11}$ | 13.5 | $4.4 \times 10^{13}$ | 1.87 | $2.37 \times 10^{10}$ | $1.27 \times 10^7$ |
| 10 " | 6.1 | 14.3 | 4.76 | 1.98 | 2.40 | 1.21 |
| 14 " | 6.6 | 15.1 | 5.15 | 2.10 | 2.45 | 1.17 |
| 18 " | 7.2 | 16.2 | 5.62 | 2.25 | 2.49 | 1.10 |
| 22 " | 7.7 | 17.0 | 6.01 | 2.36 | 2.54 | 1.07 |
| 30 " | 8.3 | 17.9 | 6.47 | 2.49 | 2.60 | 1.04 |
| 1.5 mm. glass. | 9.6 | 20.0 | 7.49 | 2.78 | 2.69 | .96 |
| .3 copper. | 11.0 | 22.2 | 8.58 | 3.09 | 2.77 | .90 |
| 0.4 zinc. | 14.0 | 27.2 | 10.92 | 3.79 | 2.88 | .76 |
| .8 " | | | | 4.60 | 2.95 (est.) | .64[1] |
| 1.2 " | | | | 5.00 | 2.97 | .59[1] |

As has already been explained, the values given in the above table will represent those for both the primary and secondary particles which are just able to penetrate through a certain absorbing layer and still cause ionization; the highest values of the velocity are those for the $\beta$-particles alone, since nearly all the secondary particles are absorbed in about 35 sheets of paper. The values of the velocity for the particles through 0.8 and 1.2 mm. of zinc could not be obtained for the reason that the limit of the available difference of potential had been reached. The values of $mV/e$ for these, however, show that the apparent mass of the particles is increasing rapidly as the velocity of light is approached. The lower limit of the $\beta$-rays cannot be stated with any certainty, but it is probably greater than $2.3 \times 10^{10}$ cm. per sec. The $\beta$-rays in all the experiments had first of all to pass through the thin glass walls of the tube, which would probably absorb about as much as the mica window.

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[1] These estimated values were extrapolated from the curve showing the relation between the velocity and $mV/e$.

The results given in the above table agree very well with those obtained by Kaufmann[1] in his later experiments, using an entirely different method, and show beyond doubt that the $\beta$-particles from radium travel with speeds approaching that of light, and further that their apparent mass does increase with the speed.

In Kaufmann's experiment secondary radiations must have been present in quantities quite comparable with the primary, and consequently any point chosen on his curved photographic traces would represent not alone the primary particle, but also some secondary particles which happened to arrive at the same point. If the primary and secondary particles differed in velocity there might possibly be some difficulty in estimating the radii of curvature for the different rays. He has compared his results with those calculated from the theoretical formulæ of Abraham, and finds a very close agreement, thus giving considerable evidence to the view that the mass of the electron is entirely electrical in origin, and increases as the speed approaches that of light. The result of the present investigation also seems to lead to the same conclusion. We must, however, remember that the confirmation of this theory is only over a short range where the increase of the apparent mass is is not very great, and where any set of values might accidently agree very closely with the theoretical. It is not until the speed has, for all experimental purposes, practically reached that of light that there is any great increase of the apparent mass, and consequently any confirmation of the theory over a long range is entirely beyond experimental means. Moreover, the assumptions made in the derivation of the theoretical fomulæ, and also in the formulæ used to calculate the velocities and ratio $e/m$ from the experimental data, are many and somewhat great. It is assumed that the same laws of electric and magnetic force apply equally well, at very high speeds, as at comparatively low, something of which we have no *à priori* knowledge. A divergence of either, or both, of these laws at high speeds could account for the experimental facts observed.

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[1] Loc. cit.

However considering all sources of error, the results of Kaufmann, together with those of the author, lend great weight to the view that the mass of the electron is electrical in origin, and increases with the speed.

## VELOCITY AND RATIO $e/m$ FOR THE SECONDARY $\beta$-RAYS.

It has been assumed in the previous sections that the velocity of the secondary rays was only slightly less than the primary, and also that they carried the same charge and had approximately equal masses. That these facts are true was proved by the following set of experiments.

The general arrangment of the experiments was the same as that used in the case of the primary rays, and the same drawings and general description will suffice here. The tube of radium, instead of being placed underneath the slit in the lead box, was shifted to one side so that no primary rays could emerge from the box. The lead box was fastened to the ebonite blocks so that the slit was near the right-hand block, and not in the middle as was the case with the primary rays. The upper lead diaphragm was removed and in its stead was fixed a strip of lead, which covered one third of the opening between the blocks. The secondary rays on emerging from the slit in the lead box could strike full upon the left-hand zinc plate, but were prevented by this strip of lead from falling upon the right-hand plate. The rest of the arrangement was precisely the same as for the primary rays, the opening at the electroscope being arranged so that no secondary rays from the lead box could enter.

The secondary rays when they strike the left-hand plate, and also the edge of the lead strip, produce tertiary rays which travel up with the secondary rays. A great part of these will be absorbed by the mica window but some will get through and cause ionization in the electroscope. There is also a small amount of secondary rays produced by the rays striking the various parts of the apparatus; these, however, do not affect the results since they come from all different parts of the vessel, and are therefore deflected very unequally.

When the electric or magnetic fields were applied in the same directions as in the case of the primary rays the same phenomena were observed; a gradual increase of ionization to a maximum with increasing fields, in one direction, and a decrease at once with the field in the other. The same absorbing layers were used in this case as in that of the primary rays. It was found that no increase of ionization above thirty layers of paper could be observed, that thickness being sufficient to almost completely absorb the secondary rays. These results confirm the idea that the secondary rays have a less penetrating character than the primary, and travel at lower speeds.

In order to estimate how far the rays were bent in the electric and magnetic fields the same method was used as for the primary rays. All that was necessary to do was to shift the tube of radium from beneath the slit in the lead box to one side so that no primary rays could get out. The soft iron screen was placed so that the rays were shielded from the influence of the field until they had passed the top of the zinc plate. The distance from the top of the zinc plate to the electroscope was less than in the case of the primary rays, but the width of the opening in the electroscope the same. The value of $mV/e$ for no absorbing layer was found to be $1.56 \times 10^3$, and for an absorbing layer of 6 sheets of paper was $1.85 \times 10^3$. These values are about the same as the corresponding ones found for the primary radiation, and show that the lower limits in the latter case were those of the secondary rays. The upper limit for the secondary rays by this method was also the same as by the other method, viz., 30 layers of paper.

Substituting these values of $mV/e$ in the results obtained by the first method we obtain 1.29 cm. as the distance through which the rays were deflected.

In this experiment, $1 = 8.4$ cm., $h = 5.5$ cm., and $d = 17.3$ cm., and therefore,

$$V = \frac{2 \times 8.4\left(\frac{8.4}{2} + 5.5\right)}{17.3 \times 17.3}\frac{X}{H} = 0.544\frac{X}{H}.$$

In the accompanying table (VII) are expressed the final results obtained for the secondary rays.

### Table VII.

| Absorbing Layer. | $X_{(\text{max.})}$ | $H_{(\text{max.})}$ | $mV/e$ | $V$ cm./sec. | $e/m$ |
|---|---|---|---|---|---|
| 0 | | | $1.56 \times 10^3$ | | |
| 6 paper. | $6.9 \times 10^{11}$ | 16 | $1.85 \times 10^3$ | $2.35 \times 10^{10}$ | $1.27 \times 10^7$ |
| 14 " | $7.5 \times 10^{11}$ | 17 | $1.97 \times 10^3$ | $2.40 \times 10^{10}$ | $1.21 \times 10^7$ |
| 22 " | $8.5 \times 10^{11}$ | 18.5 | $2.16 \times 10^3$ | $2.50 \times 10^{10}$ | $1.16 \times 10^7$ |
| 30 " | $9.6 \times 10^{11}$ | 20.2 | $2.36 \times 10^3$ | $2.58 \times 10^{10}$ | $1.09 \times 10^7$ |

It will be seen at once from this table that the values of the velocity, and ratio $e/m$, for the secondary rays are in good agreement with those obtained for the primary. Since the experiments on the secondary radiations from different substances, described earlier in this paper, showed that they were all deflected in a magnetic, and since further that the penetrating power of the rays were not greatly different, we can conclude that both metals and dielectrics give off when struck by $\beta$-rays, negatively charged particles with velocities, and ratio $e/m$, the same as those for the less penetrating $\beta$-rays.

As to the origin of these secondary and tertiary radiations, two possible explanations can be given. They might be the primary $\beta$-particles reflected back from the molecules of the bombarded substance. The other, and to me, more probable view is, that the secondary radiations are produced when the primary $\beta$-rays, striking the atoms of the substance, cause them to give off one or more of the electrons of which they are composed, with sufficient velocity to escape from the substance. The longer the path, and the greater the number of atoms which a $\beta$-particle encounters before it is absorbed, the greater will be the amount of the secondary radiation produced. The nature and amount of the secondary radiations produced will depend on the nature of the atom of the substance and on the density. The production of secondary and tertiary radiations is then similar in many respects to the production of $\beta$-rays by the radioactive substances; in the latter case the action is as far as we know spontaneous, in the former it is due to external agents.

## Conclusion.

It will perhaps be instructive to briefly summarize here the main facts brought out in the present investigation.

The difficulty experienced at first in obtaining an electrostatic deflection of the $\beta$-rays can be shown to be due mainly, I think, to the disturbing action of the secondary and tertiary radiations.

When this disturbing action had been eliminated by the later methods adopted, values of the velocity, and ratio $e/m$, were obtained which agreed closely with those found by Kaufmann using an entirely different method.

The greater part of the secondary radiations, which are produced when the primary $\beta$-rays strike upon an absorbing material, are composed of negatively charged particles travelling at speeds nearly equal to that of the $\beta$-rays themselves, and having the same ratio $e/m$ for corresponding velocities. The secondary rays themselves when incident upon a substance produce tertiary rays, which are of slightly less penetrating character, are deflectable in a magnetic field in the same direction as the secondary and primary $\beta$-rays, and are probably of the same nature as these.

The values of $e/m$ obtained for both the primary and secondary $\beta$-rays showed that the apparent mass of the particles increased as that speed approached the velocity of light.

Taking for granted that the assumptions involved in the calculations of the velocity, and $e/m$, are correct, my results together with those of Kaufmann furnish evidence in favor of the view that the mass of the electron is entirely electrical in nature.

In conclusion I wish to express my sincere thanks to Professor Ames for his kindly interest, valuable suggestions, and for the facilities which he placed at my command during the progress of this investigation.

JOHNS HOPKINS UNIVERSITY, BALTIMORE, MD.,
March, 1906.

# LIMITATIONS OF THE BALLISTIC METHOD FOR MAGNETIC INDUCTION.

By A. Hoyt Taylor.

THIS investigation is incidental to a more extended inquiry into the magnetic properties of electrolytic iron — an inquiry made possible by a grant from the Carnegie Institution to Professor C. F. Burgess, of the department of applied electrochemistry, and by the kindness of the latter in furnishing the samples of iron tested.

Very early in this investigation it became apparent that the step by step ballistic method applied to an electrolytic iron ring, gave results which were very far from being in accord with those obtained by the method of reversals. It also developed that this discrepancy, although more pronounced in the case of pure electrolytic iron, was present, in varying degrees, in nearly all samples of iron and steel available for the test. It therefore seemed worth while to investigate these discrepancies, with a view to determining their possible quantitative effect on cyclic curves of magnetization, and with the object of devising a means of eliminating them.

An examination of the literature concerning the magnetic properties of iron is too great an undertaking to be attempted in detail. It is quite evident, however, that this effect has not escaped notice. Ewing[1] notes that there are slow changes in the magnetic induction taking place some time after the field has reached a steady state, and remarks that these would cause an error where a ballistic method is used. E. Wilson[2] working with "almost pure iron" found large discrepancies between the results obtained by the method of reversals and by the step by step method.

He showed that the error came in principally in the steep parts of the hysteresis loop and that it was not a function of the time constant of his primary circuit, but was due rather to a viscous time lag of the magnetic induction behind the field. This time lag he showed was persistent and noticeable for as long as ten seconds after the changes in field strength had been made, and was of such magnitude that it could not be accounted for on the basis of the retarding effect of eddy currents. He did not vary the time constant of his circuit within very wide limits, nor did he investigate the effect of changing the period of his galvanometer. His results can hardly be extended so as to find the distortion produced in the hysteresis loop by these errors.

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[1] Magnetic Properties of Iron, etc.

[2] Proc. Roy. Soc., 62, 1898.

R. Jouaust[1] found viscous hysteresis in many soft steels, the extent of viscosity depending somewhat on the dimensions of the rings tested. He suggests that the step by step method be so modified that in running a hysteresis loop the steps be always taken from low fields to comparatively strong ones. This would eliminate magnetic viscosity, which is not evident under strong fields, but would require a rather complicated cycle of operations between observations.

Fr. Rücker[2] notes magnetic viscosity in iron and steel, and states that the step by step method gives values for the magnetic induction which are too low. I have not access to this paper, but according to a brief review of the same, no remedy for the error is suggested.

In the present case, when discrepancies were observed between the method of reversals and the step by step method, the author was at first inclined to ascribe them to peculiarities of the electrolytic iron. An investigation of two samples of laminated soft iron rings, made from armature stampings showed the same effect, though not in so marked a degree. Then two solid iron rings which had been used in the laboratory for testing purposes were tried, both showing the effect to a considerable extent. In the case of one laminated iron ring, of one square inch cross-section, with a radius of five inches, and having 1,009 turns on the primary, the method of reversals gave values for the maximum induction 47 per cent. higher than those obtained by the step by step method. This was found to be due to the fact that in certain portions of the cycle where the differential permeability was high and hence the self-induction of the primary circuit was large, the time constant of the primary circuit was so large that the primary current, and hence the field strength, did not attain to its maximum value until after the first throw of the galvanometer had taken place. The time constant of the circuit was unusually large because the resistance was low and constant, variations in primary current being made by varying the applied voltage over any desired range with a potentiometer device. This scheme was exceedingly convenient and easy of manipulation by one observer working alone, but was dropped for the reasons cited above. When a constant potential and a variable series resistance is used in the primary circuit, then at points where the differential permeability, and hence the inductance, of the primary circuit is high, the field is always low, the primary current small, and hence the series resistance large. This gives a small time constant, and an applied voltage (20 volts) was found such that any error due to slow rise of primary current was eliminated for all of the rings. This was shown by the fact that doubling the applied voltage and series resistance, hence halving the time constant, did not affect the results. In the case of all samples except one, which was hard iron with a rather large coercive force (4.00 dynes), there was still a very considerable discrepancy between the maximum induction as obtained by the two methods, the method of reversals giving invariably the greater value. In the case of the electrolytic iron, which after annealing behaves as far as I can say at present, like any soft steel, the effect was most marked, the discrepancy amounting to 17 per cent. This is undoubtedly due to magnetic viscosity, and an attempt was made to eliminate it by increasing the galvanometer period from 5.5 to 15.0 seconds. By this means the maximum inductions as determined by the two methods, were brought within 11.05 per cent. of each other. From this one may infer that the viscous effect is of such long duration that no galvanometer of sufficiently short period to be workable, would give results very nearly correct. An instrument of the fluxmeter type would be admirably suited to such cases.

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[1] Comptes Rendus, Vol. 139, pp. 272, 1904.

[2] Diss. Halle, 1905.

However, the step by step method may be so modified as to prevent these errors from being additive, and to nearly eliminate them, even with a fairly short period galvanometer. The arrangement of the apparatus is nearly the same as for the regular step by step method. The secondary coil of the ring being tested is connected in series with the galvanometer *G*, a suitable high resistance *H*, and a switch $S_4$. A damping coil and commutator, not shown in the sketch, were also included in this circuit.

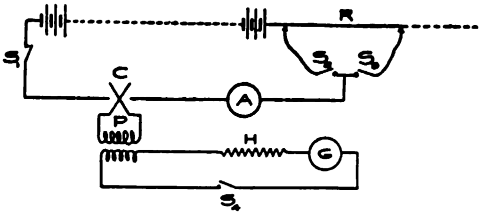

Fig. 1.

The primary coil *P* is connected through a commutator *C* and switch $S_1$ with a storage battery and an ammeter. The switches $S_2$ and $S_3$ allow more or less of the wire rheostat *R* to be put in circuit. If desired (as in the step by step method) one of the switches $S_2$ and $S_3$ may always be kept closed, and hence the current never broken. The rheostat *R* consists of I. A. wire, mostly No. 30, but with five or six ohms of No. 16 for the larger currents. The switches $S_2$ and $S_3$ connect with the rheostat by means of flexible leads and spring clip terminals, provided with copper jaws for gripping the rheostat wire firmly.

For the determination of points on the upper branch of the hysteresis loop, from saturation point to retentivity point (zero field) the method is as follows: $S_1$ is closed and $S_2$ is connected to such a point on *R* that a current flows in the primary, strong enough to produce a saturation field. In this case the current was 5.00 amperes and the field 100 dynes, which was in most cases far more than enough to cause saturation. Then $S_3$ is closed, connected to such a point on *R* that when $S_2$ is opened, the current falls to any desired valve. Then $S_4$ is closed and the galvanometer brought to rest with the damping coil. Finally, on breaking $S_1$, one observes the deflection caused by the change in induction in passing from any desired point such as *A*, for instance, in Curve I., to *O*, the retentivity point.

The observations may be repeated as often as desired, the cycle of operations being this: Open $S_4$, close $S_1$, close $S_2$, close and set on the rheostat $S_3$, open $S_2$, open $S_1$. Whatever viscous effect may be present will not cause a cumulative error as in the regular step by step method.

For the remainder of the cycle, from the retentivity point to the saturation point the change of induction is observed from the retentivity point to any point, such as $A'$, Curve I. This requires a slightly more complicated cycle of operations, since the iron must be carried back to the first or upper saturation point, and down to the retentivity point before the observation is taken. $S_3$ is set on

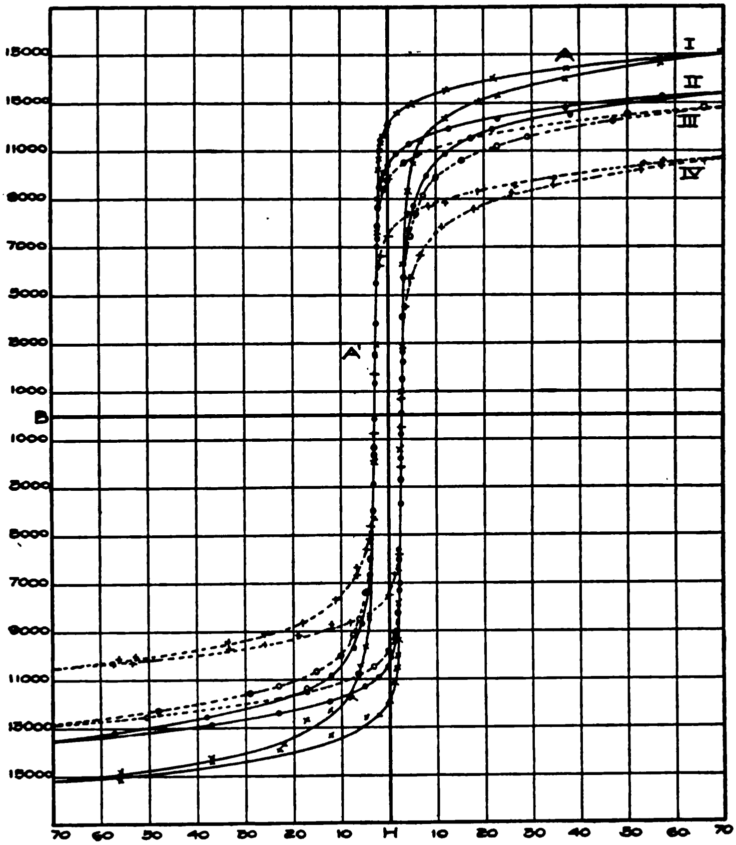

Fig. 2.

the rheostat for the current corresponding to the field strength at $A'$. The method is then as follows: Open $S_4$, reverse $C$, close $S_2$, close and set $S_3$, open $S_2$, open $S_1$, reverse $C$, close $S_4$ and close $S_1$, observing the deflection.

Curve I. was obtained in this manner, and represents what we may call the true hysteresis curve for a ring of annealed electrolytic iron of radius 4.12 cm. and area 0.7 cm.$^2$, primary winding 424, secondary 700. The period of the shielded ballistic galvanometer used was 15 sec. and the applied voltage in the primary circuit was 40 volts.

It required nearly twice as much time to run this test as it did to get Curve II., using the same apparatus and the regular step by step method. The hysteresis area of Curve II. is 18 per cent. smaller than that of Curve I.; the retentivity point is 16 per cent. lower, and the maximum induction is 11.8 per cent. lower. The coercive force is practically the same for all four curves.

Curve III. was taken exactly as was Curve II., except that the galvanometer period was 5.5 sec. and hence the viscosity causes a larger discrepancy.

Curve IV. was taken exactly as was Curve III., except that the primary resistance was kept constant and the voltage varied by a potentiometer arrangement in order to vary the primary current. As explained earlier in the paper, this gives a larger time constant and introduces another error besides the one due to viscosity.

These discrepancies are more marked as more and more steps are taken on the curves, because the errors are cumulative. They are not peculiar to electrolytic iron, but may occur in any soft steels, and in many samples of iron, even when laminated, although perhaps not to so marked a degree.

It seems clear then, that the ring tests should be done with the modified ballistic method, or better yet, if sufficient sensibility can be obtained, with an instrument of the fluxmeter type.

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# THE THERMO-ELECTRIC BEHAVIOR OF SILVER IN A THERMO-ELEMENT OF THE FIRST CLASS.

By W. D. Henderson.

## Introductory.

THE research recorded in the following pages has for its object an investigation of the thermo-electric behavior of silver, with special reference to the more general problem of the relation of heat to electromotive force. Throughout the work, three subsidiary problems have been kept in view — namely, (*a*) an investigation of the direction of the electromotive force due to a difference of temperature; (*b*) an investigation of the relation of the electromotive force due to a given difference of concentration, to that due to a corresponding difference of absolute temperature; and (*c*) an investigation of the relation of thermo-electromotive force to the concentration of the electrolyte.

For the sake of clearness in the use of terms, the following explanatory paragraphs are given:

Two electrodes of a given metal immersed in a solution of the salt of this metal, constitute a reversible element of the simplest type. Consider the cell to be of the ordinary U-form, and let the two limbs of the cell, and also the two electrodes contained therein, be represented by the symbols $A$ and $B$. Also, the cathode is that electrode *to* which the current flows in the electrolyte, or *from* which the current flows in the external circuit. A concentration cell, of the form described above, is one in which the concentration of the electrolyte in $A$ differs from that in $B$; a thermo-element is one in which the concentration is the same in both limbs, but the temperature in $A$ differs from that in $B$. An element of the first class is a cell in which the two electrodes are of the same metal, and are immersed in a solution of a salt of this metal.

Now, it is a well known fact that a difference of electromotive force may be established between the electrodes *A* and *B* in at least two ways. First, an electromotive force will result from a difference of concentration at *A* and *B*, the temperature on the two sides being the same; and second, an electromotive force will result from a difference of temperature at *A* and *B*, the concentration on the two sides being the same. An electromotive force due to a difference of temperature will be referred to as a thermo-electromotive force.

## Historical.

As early as 1825 Walker[1] experimented on the relation of heat to electromotive force. He was followed by Faraday,[2] and later by Gore.[3] All three in general used platinum electrodes, hence their results were vitiated by polarization effects. In the few cases in which electrodes of the same metal as the salt in solution were used, complex chemical reactions seriously interfered with definite results.

In 1880 Bouty[4] reported a series of tests in which he used as electrodes a number of metals immersed in solutions of their own salts. For copper, zinc, cadmium, and mercury, the warm electrode was the cathode; for iron the results were very erratic; for gold the direction of the current changed for different temperatures; for silver, nickel, magnesium and aluminium the results were variable and unsatisfactory, the cold electrode, in general, being the cathode. He concluded that the electromotive force is proportional to the change in temperature and is independent of the concentration.

Carhart[5] confirmed Bouty's results for copper and zinc, but found that the electromotive force is not independent of the concentration. His researches with reference to the change of electromotive force with change of concentration were later confirmed by Ebling,[6] who worked on cells of the type, Cu — $CuSO_4$, Zn — $ZuSO_4$, Cd — $CdSO_4$.

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[1] Pogg. Ann., 4, 327, 1825.

[2] Exp. Researches, Sr., 17, 225, 1932, 1840.

[3] Proc. Roy. Soc., 1856, and following.

[4] J. de Phys., 9, 1880; Comp. Rend., 90, 918, 1880.

[5] Carhart's Primary Batteries.

[6] Wied. Ann., 30, 130, 1887.

Nernst,[1] using mercury electrodes in a thermoelement of the type, $Hg - Hg_2Cl_2 - HCl - Hg_2Cl_2 - Hg$, found the warm electrode to be the cathode.

In 1894 Hagenbach[2] repeated the experiments of both Bouty and Ebling. His results for copper, zinc and cadmium agreed well with those of Ebling. In many particulars, however, his results did not agree with those of Bouty. For example, in the case of $Ni - NiSO_4$, Bouty reported that the cold electrode was the cathode. Hagenbach repeated the experiment, and reported that no definite results were attainable. He also reported that silver electrodes in solutions of silver salts gave unreliable results.

In connection with his thermo-electric theory of concentration cells, Carhart[3] investigated the electromotive force of cells of the following types: $Zn - ZnSO_4 - Zn$, Zn Amal. $- ZnSO_4 -$ Zn Amal., $Ni - NiSO_4 - Ni$. He called attention to the relation between the concentration of the electrolyte and the thermo-electromotive force, and also its import when applied to the Helmholtz equation for electromotive force.

McClellan[4] in 1903, and Meyer[5] the following year, worked on the problem of the thermo-electromotive force of nickel nitrate. Both, however, used platinum electrodes, hence obtained unsatisfactory results due to polarization effects.

It may be noted in this connection that the Peltier effect, both at the surface of contact of a metal and a solution, and at the surface of separation of two electrolytes, has been measured by a number of investigators,[6] who have shown that in general the same laws appear to hold as in the case of metals.

## Discussion of the Problem.

The Gibbs-Helmholtz equation for electromotive force is based on fundamental principles of thermo-dynamics; the Nernst equation is derived from the conception of solution pressure and osmotic pressure as applied to the electrode and electrolyte of a cell. The former is, mathematically speaking, the more rigid of the two; the latter, however, lends itself, within certain limits, more readily to experimental demonstration. In the Nernst equation the electromotive force is expressed as a function of the solution pressure of the metal, the osmotic pressure of the solution, and the temperature. It assumes the application of the gas laws, and takes no account of sources of electromotive force other than those mentioned above. A general expression of this equation is as follows:

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[1] Zeit. f. Phys. Chem., 4, 169, 1889.

[2] Wied. Ann., 53, 1894.

[3] Trans. Am. Electrochem. Soc., 1, 1, 1902; 2, 123, 1902.

[4] Phys. Rev., 17, 255, 1903.

[5] Phys. Rev., 19, 156, 1904.

[6] (*a*) Pogg. Ann., 13, 467, 1870; (*b*) Wied. Ann., 9, 573, 1880; (*c*) Ann. de Chim. et Phys., (7), 3, 83, 1894.

$$E = \frac{R}{Kn}\left[T_1 \log \frac{P_1}{p_1} - T_2 \log \frac{P_2}{p_2} + T_3 \frac{u-v}{u+v} \log \frac{p_1}{p_2}\right]. \qquad (1)$$

$E$ represents the resultant electromotive force of the cell; $T$, absolute temperature; $R$, the gas constant; $K$, 96,540 coulombs; $n$, valence; $P$, solution pressure of the metal; $p$, osmotic pressure of the solution; $u$ and $v$, migration velocities of the ions.

When $P_1 = P_2$, and $T_1 = T_2 = T_3$, equation (1) may be written

$$E = \frac{RT}{Kn}\left[\frac{2v}{u+v}\right] \log \frac{C_1}{C_2}, \qquad (2)$$

in which the ratio of concentrations, $C_1/C_2$, is set equal to the ratio of osmotic pressures, $p_1/p_2$.

Nernst has proved that under certain conditions, as in the case of Ag — $AgNO_3$ concentration cell, the calculated values, obtained by means of equation (2), agree remarkably well with the observed values.

Now, the question arises, how far can this proof be extended under other conditions of the variables $T$ and $p$? That is to say, how far, for example, will the conception of solution pressure and osmotic pressure, as applied to the concentration cell, explain the phenomena of a thermo-element of the first class?

The results of investigation thus far, with respect to the relation of heat to electromotive force, may be collected under three heads as follows: First, work done with polarizable electrodes; second, work done with unpolarizable electrodes in cells of the second class — that is, cells of the type, $Hg - Hg_2Cl_2 - HCl - Hg_2Cl_2 - Hg$;

and third, work done with unpolarizable electrodes in the cells of the first class — namely, of the type, Zn — $ZnSO_4$ — Zn. It is to phenomena connected with cells of the last named group that this paper invites attention, since in cells of this class are found the simplest possible conditions and the fewest disturbing factors.

The writer is perfectly well aware that the mere tabulation of data does not offer a solution to the problem. Before such data can be of much value we must have pretty definite information regarding the physical condition of the electrodes, the nature of the electrolyte, and what occurs when these component parts of the cell are combined. If, for example, the electrodes are oxidized, or contain occluded gases, or become polarized, variable and unsatisfactory results will necessarily follow. Or, again, if in the case of the electrolyte, unknown and complex physical or chemical changes occur in the process of solution, little can be expected in the way of definite results.

Assuming now that the above-named conditions can be fairly well satisfied, let us consider for a moment the relation of $E$ to the variables $T$ and $p$ (absolute temperature and osmotic pressure). If in the U-shaped cell previously mentioned the electrolyte be of uniform concentration, and the electrode $A$ be brought to a temperature higher than $B$, then $p$ in limb $A$ will be greater than that in limb $B$, since the osmotic pressure varies as the absolute temperature. Then, assuming that the solution pressure, $P$, does not change, and assuming also that no other factors enter in, the resulting electromotive force will be directed *in the electrolyte* from the cold electrode to the warm; that is to say, the warm electrode will be the cathode. If, however, the cold electrode prove to be the cathode, then it will be necessary to revise our assumptions, or look for other factors as a source of electromotive force, in addition to those already named.

Also, since $E$ is a function of $p$, and $p$ in turn is a function of both $T$ and $C$, it is possible to vary $p$, and therefore $E$, by varying either the absolute temperature $T$, or the concentration $C$.

Now, if the conditions be chosen such that $T_1$ (equation 1) be equal to $T_2$, and $p$ be varied through a series of values, $y_1$, $y_2$, etc., by making $C_1$ greater or less than $C_2$, a resultant electromotive force, $E'$, will be observed in accordance with the well-known laws of the concentration cell. Suppose, further, that $C_1$ be made to equal $C_2$ (equation 2) and $p$ be varied now through a calculated series of values, $y_1, y_2$, etc., as above, by making $T_1$ greater or less than $T_2$, again there will result an electromotive force, say $E''$. How will $E''$ compare with $E'$, previously obtained? Theoretically, the two values should be the same. In case a difference in value between $E'$ and $E''$ be found, and such difference be greater than that due to experimental error, then again we must revise our assumptions, or look for some additional factor as a source of electromotive force.

Then, to summarize, in considering an element of the first class in connection with the subject of the relation of heat to electromotive force, three important questions arise. First, do all metals immersed in solutions of their own salts, under conditions as described, give a current through the electrolyte from the cold to the warm portion — that is, is the warm electrode the cathode? Second, how does the electromotive force resulting from osmotic pressure changes, due to a given difference in concentration, compare with the electromotive force resulting from osmotic pressure changes, due to a corresponding difference in absolute temperature? And third, in a thermo-element, what is the relation between the concentration of the electrolyte and the resulting thermo-electromotive force? In other words, to summarize all three questions, under varying conditions of the temperature, will the factors of solution pressure and osmotic pressure account for the observed electromotive force?

The answer to these questions involves the working out of a large and complex problem, the solution of which requires much more extended research than comes within the limits set for this paper. The following investigation has to do mainly with the thermo-electric behavior of silver, and has been prosecuted with the hope that some further light may be thrown on the general problem of the relation of heat to electromotive force.

## APPARATUS.

The following is a brief and general description of the apparatus used, special pieces, such as electrodes, etc., being described later in connection with the experiments.

Two thermostats were employed, and are shown in outline in Figs. 1 and 3. Temperature measurements were made by means of Beckmann thermometers, reading directly to hundredths of a degree.

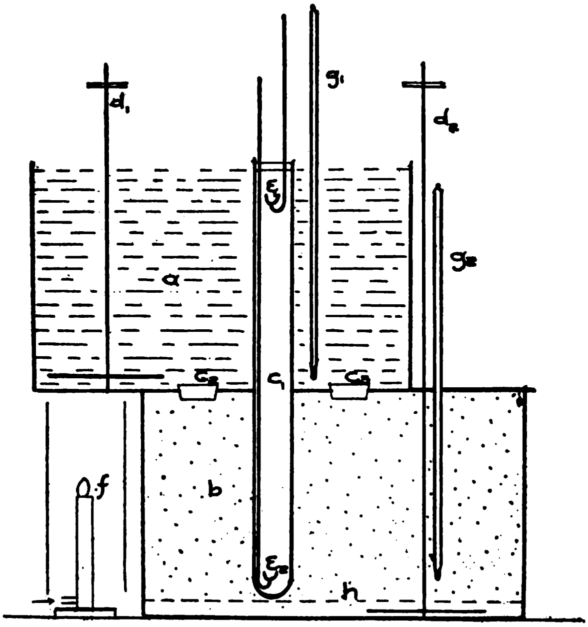

Fig. 1.

The temperature in the warm bath was held constant to within a few hundredths of a degree by means of large toluene-mercury regulators. In the thermostat shown in Fig. 1, the ice bath was in the lower chamber; in the case of that shown in Fig. 3, the ice bath consisted of a large Dewar flask enclosed in a jacket of building. felt. In the thermostat shown in Fig. 1, a stirrer was used in both chambers; in that shown in Fig. 3, a stirrer was used only in the warm bath.

Measurements of electromotive force were made by means of an Otto Wolff potentiometer which reads directly to 0.00001 volt. A Leeds and Northrup galvanometer was employed of such sensitiveness that a change of 0.00001 volt gave a deflection of one scale part, at a distance of ten feet. The electromotive force to be measured was balanced against that of a standard cadmium cell.

## EXPERIMENTS AND RESULTS.

A preliminary test was made with reference to the direction of the electromotive force of a number of metals when immersed in solutions of their own salts. A large H-formed cell was employed, the cross-tube of which contained a stop-cock. During the test, one leg of the cell was kept in a 25° bath; the other, in ice. The following types of reversible cells were used: $Zn - ZnSO_4 - Zn$; $Cd - CdSO_4 - Cd$; Cd Amal. $- CdSO_4 -$ Cd Amal.; $Hg - HgNO_3 - Hg$; $Ag - AgNO_3 - Ag$.

In the case of zinc, cadmium, cadmium amalgam and mercury, the warm electrode was the cathode; in the case of silver, the cold electrode was the cathode.

A more pretentious piece of apparatus was now constructed, and a more thorough investigation of the direction of the electromotive force of silver undertaken. Fig. 1 represents in outline the containing baths, cells, and auxiliary apparatus. The warm bath (*a*) was kept at a temperature of 25°; the cold bath (*b*) about zero. Cell ($c_1$) consisted of a cylindrical glass tube 60 cm. in length, and about 5 cm. in diameter. Two stirrers were provided, $d_1$ and $d_2$, the latter working in the cold water below the ice. The flame (*f*) was controlled by a regulator not shown in the cut. It was easily possible to hold the temperature constant in either bath to within a few hundredths of a degree. It may be well to remark here that this particular piece of apparatus was devised with two objects in view — namely, (*a*) the investigation herein described, and (*b*) an investigation of the so-called Soret phenomenon, for the accomplishment of which the apparatus is admirably adapted. Openings between the chambers (*a*) and (*b*), Fig. 1, were provided for five cells similar to ($c_1$), three such being shown in the cut.

The electrodes ($E_1$) and ($E_2$) deserve special mention. At the beginning of the work great difficulty was experienced in getting electrodes that would give anything like zero initial values. What was required were electrodes that would give zero readings to nearly the fifth decimal place, and second, electrodes that would give reproducible and constant values for several days or weeks. As already stated, unusual difficulties were met with in attempting to fulfill these conditions. Electrodes prepared from the same piece of metal, under apparently the same conditions, would sometimes give an initial electromotive force of as high as 0.003 to 0.005 volt. And again, after electrodes were obtained that would give the required initial reading, it was found that they would not remain constant for any length of time, going now to positive values, and again to negative, in a most hopeless and discouraging manner. In view of the difficulties just mentioned, it is not at all surprising that Bouty and Hagenbach spoke of silver as "variable" and "unreliable."

The first difficulty encountered was in sealing the electrode to the glass supporting tube. In a few cases it was possible to seal fine silver wire directly into the glass, but in most cases this failed. After a test extending over a period of two or three months, all methods of sealing in with wax in any form were abandoned. Such electrodes in a solution of silver nitrate invariably "broke down" — that is, they eventually gave erratic and variable results, due to the action of the solution upon the wax. Electrodes prepared by depositing, electrolytically, silver on clean platinum spirals gave fairly good results, so far as constancy was concerned, but it was found that two sets of electrodes prepared in exactly the same manner, and immersed in the same solution would often give widely different results.

The electrodes finally made use of were prepared after the following manner: From the purest obtainable chemicals, silver chloride was precipitated. The chloride was filtered out, washed and then dissolved in ammonium hydroxide, and from this solution the silver was precipitated by means of pure electrolytic copper. The precipitated silver was now digested in excess of ammonia, after which it was thoroughly washed. The final product consisted of a fine grayish powder, which will be referred to hereafter as "precipitated silver." The complete form of this electrode is shown in Fig. 2. The precipitated silver, just described, was placed in the cup (*j*). A long silver wire (*m*) was fused to a short platinum wire (*k*) at (*l*). The platinum wire, in turn, was fused through the glass as shown, the point which protruded into the cup (*j*) being silver plated, thus making electrical contact with the metal of the electrode proper. In one case, hereafter mentioned, no platinum wire was used, the silver wire (*m*) being fused through the cup at (*j*). With such electrodes, except that the form was modified later on, all the results recorded with reference to silver were obtained. It was found possible to obtain zero initial readings to nearly the fifth decimal place, and further, not only did different sets of electrodes give concordant results, but the values showed remarkable constancy over a relatively long period of time.

Nothing new is claimed for the above method for the preparation of silver, or for the use of finely divided metal as an electrode.[1] The details are given because, of the many methods suggested, the foregoing gave the most satisfactory results.

Cell (*c*) (Fig. 1) was now filled with a tenth normal solution of silver nitrate. Both electrodes ($e_1$) and ($e_2$), were placed near the top of the cell (Tem. 25°), and the initial electromotive force observed. Electrode ($e_2$) was then lowered to the bottom of the cell (Tem. near 0°), and observations were taken over a period of twenty days.

The object of this test was threefold, namely (*a*) to note the direction, (*b*) the constancy, and (*c*) the conditions attending the resulting electromotive force over a considerable period of time.

The results of the test are embodied in Table I.

In considering Table I., it is to be noted that the cold electrode remained the cathode throughout the experiment, and that the electromotive force was remarkably constant. Further the elimination of oxygen from the electrolyte by exhaustion, and then saturating the solution with nitrogen, seemed to produce no notable change in the values observed. After exchanging the electrodes, the electromotive force was 0.00030 volt higher than before the change. This small difference might be accounted for by the fact that at the close of the experiment it was found that one of the glass tubes of the electrodes was slightly cracked, allowing a little of the solution to come in contact with the silver wire (*m*) (Fig. 2).

It was now thought desirable to repeat the experiment recorded in Table I., and to extend the test to other metals. The object here was to compare silver, mercury, and cadmium amalgam under similar conditions, and also to see if the "Soret effect" entered into the problem. By the "Soret effect" is meant the production of a

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[1] Richards and Lewis in Zeit. f. Phys. Chem., 28, 8.

TABLE I.

| Date. | $T_1-T_2$ | E.M.F. | Notes. |
|---|---|---|---|
| Feb. 25, 8 A. M. | 0.0 | 0.00006 | Initial condition of electrodes. Bath at $25^{C}$. Electrode *A* at top. Temperature = 25°. Electrode *B* at bottom. Temperature = 0°. Cold electrode cathode (+). |
| " 25, 11 " | 24 | 966 | |
| " 25, 8 P. M. | 23.75 | 961 | |
| " 26, 8 " | 23.5 | 960 | |
| " 27, 8 A. M. | 23.9 | 963 | |
| " 27, 12 " | 23.7 | 965 | |
| " 28. | 23.5 | 966 | |
| March 1. | 23.3 | 967 | |
| " 2, 8 A. M. | 23.5 | 965 | |
| " 2, 1 P. M. | 23.6 | 968 | |
| " 2, 9 " | 23.7 | 966 | |
| " 3. | 23.6 | 964 | The electrodes were now exchanged — electrode *A* was put at bottom; *B* at top. *A* changed from — to +; that is, the cold electrode again became the cathode. |
| " 3. | 23.7 | 0.00130 | |
| " 4. | 23.6 | 1071 | |
| " 5. | 23.8 | 1045 | |
| " 6. | 23.6 | 1022 | |
| " 7. | 23.7 | 1002 | |
| " 8. | 23.7 | 977 | Had trouble here with motor; water in bath not well stirred. |
| " 9. | 23.6 | 977 | |
| " 10. | 23.7 | 975 | |
| " 10, 2 P. M. | 23.8 | 990 | From this time on the solution in the cell was saturated with pure nitrogen. |
| " 10, 9 " | 23.7 | 993 | |
| " 11. | 23.6 | 998 | |
| " 12. | 24.5 | 980 | |
| " 13. | 23.6 | 991 | |
| " 14. | 23.8 | 992 | |
| " 16. | 23.7 | 995 | |
| " 17. | 23.9 | 998 | |

difference of concentration in the cell due to the difference in temperature. The solution at the top of the cell ($c_1$), Fig. 1, was at a temperature 25° higher than that at the bottom. This difference of temperature would produce, at the outset, a corresponding difference of osmotic pressure, the greater pressure being at the top. According to the theories embodied in an explanation of the Soret phenomenon,[1] however, equilibrium in the cell would eventually be established by an osmotic pressure at the bottom of the cell (the cold portion) due to an increase of concentration, equal to that at the top, due to the increase of temperature. In other words when the contents of the cell came to equlibrium, the solution should show an increase of concentration at the bottom (the cold portion) proportioned to the difference of absolute temperature between the two extremities of the cell.

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[1] Ann. de Chim. et Phys. (5), 22, 293, 1881.

Two new cells ($c_2$ and $c_3$), Fig. 1, were now put into the bath in a manner similar to that of $c_1$. The three cells were of the following types: $Ag - AgNO_3$; Cd Amal. — $CdSO_4$; $Hg - HgNO_3 + HNO_3$.

The silver electrodes were similar to those described in connection with Table I. In this case no platinum wire was used in the construction of the electrode, the silver wires being fused into the glass at (*k*), Fig. 2. Long wires were used to avoid any possibility of a thermo-electromotive force of metallic contact.

The cadmium amalgam electrodes were, in outline, similar to that shown in Fig. 2. In this case, however, the cup (*j*) was filled with twelve and a half per cent. cadmium amalgam. The tube (*i*) was also filled with amalgam, which made electrical contact with (*j*) by means of a short platinum wire (*k*). The platinum wire was so short that there was no possibility of a resultant electromotive force of metallic contact, since in both electrodes there could be no difference of temperature at the ends of the wire.

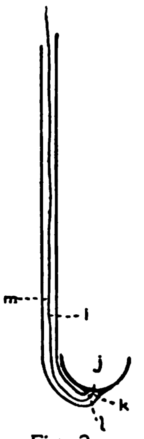

Fig. 2.

The mercury electrodes were prepared in a similar manner.

In the case of the electrolyte, a tenth normal solution was used in each of the cells. Just enough nitric acid was added to the mercury cell to hold the mercurous nitrate in solution.

After the experiment had been in operation seven days, analyses for concentration changes at the electrodes were made several times a day. By means of a long capillary pipette a small quantity of the electrolyte of a given cell was drawn off from the cold and the warm portions, and tested for concentration changes by conductivity methods.

A record of the experiment follows in Table II.

TABLE II.

| Date. | $T_1-T_2$ | *Ag* *Cold El.* + | *Cd Amal.* *Hot El.* + | *Hg* *Hot El.* + | Notes. |
|---|---|---|---|---|---|
| May 20 | 0.0 | 0.00008 | 0.00012 | 0.00000 | Both electrodes at 30°. |
| " " | 29.95 | 1105 | 1184 | 340 | |
| " 21 | 30.00 | 1234 | 1157 | 338 | |
| " " | 30.00 | 1264 | 1162 | 350 | |
| " 22 | 29.97 | 1270 | 1163 | 352 | |
| " 23 | 30.02 | 1278 | 1173 | 363 | |
| " 24 | 30.03 | 1278 | 1176 | 366 | |
| " 25 | 30.01 | 1279 | 1174 | 364 | |
| " 26 | 30.00 | 1284 | 1168 | 368 | |
| " 27 | 29.90 | 1276 | 1179 | 368 | Analysis was begun here. |
| " 28 | 29.92 | 1266 | 1183 | 374 | |
| " 29 | 29.97 | 1278 | 1194 | 372 | |
| " 30 | 30.00 | 1281 | 1195 | 384 | |

Analyses during the progress of the experiment recorded in Table II. showed no changes of concentration at the electrodes — in other words, showed no evidence of the Soret phenomena. This was probably due partly to the length of cell used (60 cm.), and also to the fact that sufficient time had not elapsed for such a change to make itself manifest. A further investigation of the Soret phenomenon will be made with the apparatus just described and shown in outline by Fig. 1.

In the case of silver, the cold electrode remained the cathode. For cadmium and mercury the warm electrode was the cathode.

Silver and cadmium gave remarkably constant values.

A careful investigation was now begun with reference to the physical character of the electrode in the case of silver. The test was qualitative in character and included cells of the types, Ag — $AgNO_3$; Ag — $AgClO_4$.

The large H-form cell, used in the preliminary tests, was employed. One leg was kept at a temperature of 25° ; the other at the temperature of the ice bath. After each test the electrodes were reversed with respect to the warm and the cold sides of the cell and new readings taken.

The silver wire described in the tests was prepared as follows: Silver was deposited electrolytically, and the product was fused and run into sticks, which in turn were drawn into wire. This wire when freshly drawn was very brittle, but when slightly annealed became very soft and pliable. The other forms used were (*a*) silver deposited on platinum, (*b*) silver cleaned in dilute nitric acid, (*c*) precipitated silver, as previously described.

The conditions, under which the tests were carried out, and the results are given in Table III.

TABLE III.

| Test No. | Condition of Electrode. | Result. |
|---|---|---|
| 1 | Freshly drawn silver wire—Unannealed—Brightly polished. | Cold electrode, cathode. |
| 2 | Freshly drawn silver wire—Annealed in Bunsen flame—Brightly polished. | " " |
| 3 | Freshly drawn silver wire—Annealed in an atmosphere of pure nitrogen by means of an electric current. | " " |
| 4 | Freshly drawn silver wire—Cleaned in dilute nitric acid. | " " |
| 5 | Silver deposited from tenth normal solution of silver nitrate on platinum spiral. | " " |
| 6 | Silver deposited on platinum spiral from standard cyanide silver-plating solution. | " " |
| 7 | Heavy deposit of silver, prepared as in (5), and cleaned in 50 per cent. solution of nitric acid. | " " |
| 8 | Precipitated silver, as previously described. | " " |

It thus appears from the preceding tables that silver in a neutral solution of $AgNO_3$ or $AgClO_4$, as a thermo-element, gives for a difference of temperature between 0° and 30°, an electromotive force directed in an opposite sense to that of zinc, copper, cadmium and mercury.

The second part of the investigation was now taken up, namely, an investigation of the relation between concentration changes and corresponding temperature changes, in the production of electromotive force. As a preliminary step, a few tests were made with reference to the temperature coefficient of a concentration cell of the type, $Ag - AgNO_3 - Ag$. According to the formula used in the calculation of the electromotive force of such a cell, the E.M.F. should vary directly as the absolute temperature, the difference in concentration remaining constant and the temperature being the same on both sides.

The H-form of cell, previously mentioned, was employed, and precipitated silver was again used as electrodes. No attempt was made to carry the experiment to any great length, it being required merely to show that under the conditions assigned, no abnormal changes occurred.

Summary of results given in Table IV.

Table IV.

| Cell No. | $C_1/C_2$ | Cond. of Electrodes. | Calc. E.M.F. | Obs. E.M.F. |
|---|---|---|---|---|
| 1 | 5.260 | Both electrodes at 30°. | 0.04564 | 0.04500 |
| 1 | " | Cell placed in ice bath. T. = 0.06°. | 0.04149 | 0.04000 |
| 1 | " | Cell again placed in 30° bath. | 0.04564 | 0.04540 |
| 1 | " | Cell again at 0.06°. | 0.04149 | 0.04174 |
| 2 | 1.596 | Temp. = 30°. | 0.01291 | 0.01310 |
| 2 | " | Temp. = 1.25°. | 0.01174 | 0.01223 |
| 3 | 1.670 | Temp. = 30°. | 0.01408 | 0.01432 |
| 3 | " | Temp. = 0.06°. | 0.01282 | 0.01260 |

The apparatus used in this part of the work is shown in Figs. 3 and 4. The cell employed was of the three-legged form, two limbs ($A_1$ and $A_2$) being kept in the warm bath, the remaining limb ($A_3$) in the ice bath. $A_1$, $A_2$ and $A_3$ were connected by means of siphons each of which contained a stop-cock.

The method of procedure was as follows: A neutral tenth normal solution of silver nitrate was put into all three cells. Cells $A_1$ and $A_2$ combined were designed to act as a concentration element; cells $A_2$ and $A_3$ to act as a thermo-element. Due to the difference of temperature between $A_2$ and $A_3$ there resulted an electro-

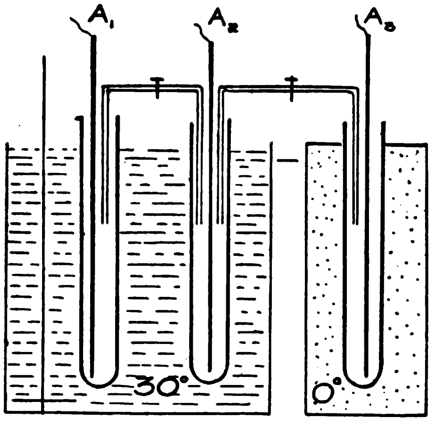

Fig. 3.

motive force, the ratio of the absolute temperatures of the two sides being 303 : 273, or 1.11. With this combination the cold electrode was as usual the cathode. The next step was to vary the concentration in $A_1$ through a series of values, thus giving a series of E.M.F. readings due to the difference of concentration between $A_1$ and $A_2$. The object was to find what concentration ratio was required to produce an electromotive force equal to that due to an absolute temperature ratio of 1.11.

In the preliminary tests the electrodes used were prepared by electrolytically depositing silver upon platinum spirals. The results obtained with this form of electrode were not entirely satisfactory. In the final test in this case, and in all subsequent tests, the precipitated silver electrodes were used to the exclusion of all others.

The form of electrode used in the final test is shown in Fig. 4. A long silver wire (*p*) was fused to a very short platinum wire (*r*), which in turn was sealed into the lower portion of the tube (*t*) in such a manner that the point (*s*) projected out of the side of the tube a few millimeters from the end. This was to prevent the silver-plated point (*s*) from being injured on the bottom of the cell.

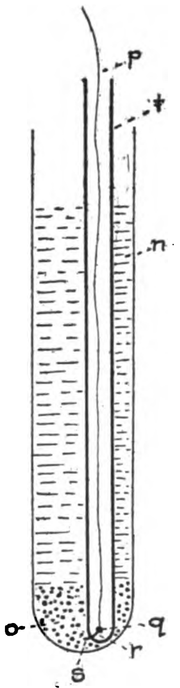

Fig. 4.

To set up the cell, precipitated silver to the depth of one or two centimeters was put into each limb ($A_1$, $A_2$ and $A_3$). A given solution of silver nitrate was then added *and the contents of each cell thoroughly shaken.* The tubes containing the conducting silver wires were now put into the cell, as shown in Fig. 4, the silvered point (*s*) making electrical contact with the precipitated silver. The cells were now put into their respective baths and connected by means of the two siphons, as shown in Fig. 3.

A thermo-electromotive force at once resulted between $A_2$ and $A_3$, due to a difference of temperature of 30°. $A_1$ and $A_2$, on the other hand, being of the same temperature and concentration, were in equilibrium to begin with. Now, as in the preceding test, the concentration in $A_1$ was varied through a series of values by the following method: After each reading the stop-cock between $A_1$ and $A_2$ was closed, and $A_1$ was taken from the bath. A small quantity of the electrolyte of limb $A_1$ was removed by means of a pipette, and a corresponding amount of water was added. The cell was then thoroughly shaken, the special form of electrode just described making this operation possible. This agitation of the electrode is quite necessary when it is desired to vary the concentration of the electrolyte through a series of values. Cell $A_1$ was now returned to its former position and allowed to come to the temperature of the bath.

The conductivity of the electrolyte in $A_2$ was taken once for all; that in $A_1$ was taken after each dilution. From this data the relative concentrations in $A_1$ and $A_2$ were obtained. The ratio $C_1 : C_2$, as used in the following table, represents a ratio of molecular conductivities. For each variation of the concentration in $A_1$ the value of the resulting electromotive force between $A_1$ and $A_2$ was calculated by means of equation (2), the data for the values of $u$ and $v$ being obtained from the Kohlrausch and Holborn tables. The object here of comparing the observed with the calculated values was to see how closely, under the conditions, the gas laws applied. In making the solutions described above, water prepared for conductivity purposes was used.

For tabulation of results of the foregoing tests see Table V.

Table V.

*Comparison of the electromotive force due to a given difference of absolute temperature, with that due to a corresponding difference of concentration. For outline of cell, see Figs. 3 and 4.*

| $C_1/C_2$ | $T_1/T_2$ | **Obs. E.M.F.** | **Calc. E.M.F.** | $C_1/C_2$ | $T_1/T_2$ | **Obs. E.M.F.** |
|---|---|---|---|---|---|---|
| 1.114 | 1 | 0.00284 | 0.00291 | 1 | 1.11 | 0.01408 |
| 1.388 | 1 | .00813 | .00910 | 1 | 1.11 | 0.01408 |
| 1.533 | 1 | .01093 | .01174 | 1 | 1.11 | 0.01408 |
| 1.710 | 1 | .01360 | .01475 | 1 | 1.11 | 0.01408 |
| 1.883 | 1 | .01615 | .01740 | 1 | 1.11 | 0.01408 |

It will be noted in connection with Table V., first, that the observed values agree fairly well with the calculated values, the difference always being in the right direction; and, second, that the electromotive force due to a difference of absolute temperature represented by the ratio 1.11 is more than five times as great as that due to a corresponding difference of concentration.

Certain results obtained with the cells just described led the writer to suspect that the thermo-electromotive force in the case of silver is a certain function of the concentration of the electrolyte, as well as of the temperature. A preliminary test was made with reference to this subject. The cell used consisted of the $A_1$ and $A_2$ limbs as shown in Fig. 3. $A_1$ was kept at a temperature of 30°; $A_2$ at 0°, or thereabouts. A solution of a given concentration was placed in the cell, after which both electrodes were thoroughly agitated. The limbs of the cell were adjusted in their respective baths, and after the electromotive force had risen to a constant value, a reading was taken. The operation was then repeated with a different concentration. The thermo-electromotive force decreased with an increase of concentration of the electrolyte, as shown by Table VI., and also by Curve I., Fig. 5, which was plotted from the values of this table.

Later the test was repeated, great care being exercised in the preparation of the electrodes. A sufficiently large quantity of the precipitated silver was used to allow for a series of tests extending over that portion of Curve I., Fig. 5, which showed the most marked change of electromotive force. The precipitated silver was thoroughly washed, and dried at a temperature of about 50°. The method of procedure was as follows: Precipitated silver to the depth of one to two centimeters was placed in the bottom of each limb of the cell ($A_2$ and $A_3$, Fig. 3). A solution of $AgNO_3$ of a given concentration was then poured into the limbs $A_2$ and $A_3$ until each was about two thirds full. The contents of each limb was then thoroughly shaken, after which the conducting tubes (*t*) were put in place, as shown in Fig. 4. The powdered silver, which had been thoroughly incorporated with the solution in the process of shaking, quickly settled to the bottom of the tube. The two limbs were now connected by means of the siphon (Fig. 3) and the cell was then placed in position in the bath, one limb being at 25° and the other at 0°. When the thermo-electromotive force came to a constant value a record was made.

After the test, the solution was poured out of the cell, and the precipitated silver composing the electrodes was removed. *A new portion* of the silver originally prepared was then placed in the cell, a solution of a different concentration added, and the process was repeated exactly as described above. Thus in each test practically new electrodes were employed. Three separate tests were made, each including the following concentrations: *n*/80, *n*/40, *n*/20, *n*/10. One test made with an *n*/160 solution showed very little increase in value over that of the *n*/80 solution; likewise, an *n*/5 solution gave a value only slightly below that of the *n*/10 solution. The values obtained by the three series of tests agree remarkably well with each other, as shown by Table VII. Curve II., Fig. 5, is plotted from the mean value column of this table.

## Table VI.

| Conc. | Cell $A_1A_2$ (Fig. 3). | | | | Cell $A_2A_3$ (Fig. 3). | |
|---|---|---|---|---|---|---|
| | $C_1/C_2$ | $T_1/T_2$ | Obs. E.M.F. | Calc. E.M.F. | $T_1-T_2$ | Obs. E.M.F. |
| *n*/10 | 1.064 | 30/30 | 0.00165 | 0.00170 | 30° | 0.01253 |
| *n*/20 | 1.200 | 30/30 | 507 | 501 | 30 | 1450 |
| *n*/40 | 1.215 | 30/30 | 513 | 530 | 30 | 1720 |
| *n*/60 | ...... | ...... | ...... | ...... | 30 | 1823 |
| *n*/80 | ...... | ...... | ...... | ...... | 30 | 1850 |
| *n*/100 | ...... | ...... | ...... | ...... | 30 | 1864 |

## Table VII.

| Conc. | $T_1-T_2$ | Test 1. | Test 2. | Test 3. | Mean E.M.F. |
|---|---|---|---|---|---|
| *n*/80 | 25° | 0.01480 | 0.01450 | 0.01440 | 0.01457 |
| *n*/40 | 25 | 0.01354 | 0.01370 | 0.01330 | 0.01351 |
| *n*/20 | 25 | 0.01260 | 0.01230 | 0.01252 | 0.01246 |
| *n*/10 | 25 | 0.01106 | 0.01106 | 0.01140 | 0.01127 |

Curves I. and II. (Fig. 5) show a fairly good agreement. It must be kept in mind that the values represented by Curve I. are due to a difference of temperature between the two limbs of the cell of 30°; while those represented by Curve II., are due to a difference

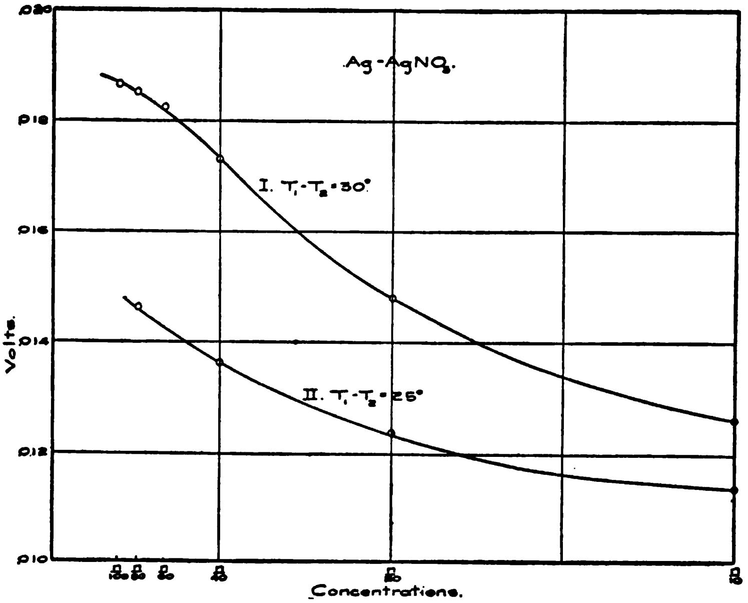

Fig. 5.

of 25°. Both indicate a maximum decrease of thermo-electromotive force between the values of one eightieth and one tenth normal.

Similar concentration curves for zinc sulphate and nickel sulphate show an *increase* of thermo-electromotive force with an increase of concentration. Such a curve for Zn — $ZnSO_4$, prepared in 1902

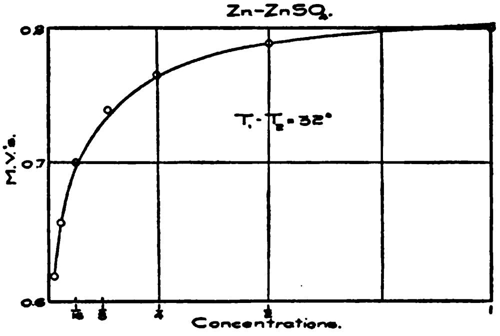

Fig. 6.

by Professor H. S. Carhart,[1] and used in the present case through his courtesy, is shown in Fig. 6. It will be noted that the curve for silver differs from that of zinc not only in direction but also in general form. This latter difference, however, is due to the portion of the respective curves chosen in plotting, and is not an intrinsic difference. The important point of the comparison lies in the difference of direction of the two curves.

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[1] Trans. Am. Electrochem. Soc., 2, 123, 1902.

## SUMMARY.

In a thermo-element of the first class, in the case of zinc, copper, cadmium and mercury, the warm electrode is the cathode. In the case of silver, on the other hand, the cold electrode is the cathode. The tests to which silver was subjected indicate that this phenomenon is not due to some peculiar property of a special electrode, since many different forms and conditions of the metal were used, and always with the same result. Cells from which the air had been thoroughly removed gave results in accord with those noted; indeed, the removal of air did not appear to affect the resulting electromotive force, either in direction or magnitude. And further, not only was the thermo-electromotive force due to a difference of 25° to 30° constant during a relatively long period of time, but also the electrodes employed gave no evidence of being changed in any respect by this difference of temperature. For example, two electrodes, prepared as described, gave, when at the same temperature, an initial reading of zero to nearly the fifth decimal place. They were then subjected to a difference of temperature of 25° for ten days, after which they were brought back to the initial condition, when both electrodes again gave practically a zero reading.

In the second place, in the case of silver, the resultant electromotive force, due to a given difference of absolute temperature, is more than five times as great as the computed osmotic pressure changes would require. Table V. shows that with a given solution, a difference of concentration represented by the ratio $C_1 : C_2$ of 1.114 gave an electromotive force of 0.00284 volt, the calculated value being 0.00291 volt; while a corresponding ratio difference of absolute temperature gave an electromotive force of 0.01408 volt, a value five times as great. When we recall that this thermo-electromotive force is directed, in the external circuit, from the cold electrode to the warm, and that no account is taken of a diminution of ionic concentration on the cold side, due to a reduction of temperature, the result appears all the more remarkable. Theoretically, from a consideration of the increase of osmotic pressure with increase of temperature, as well as the increase of ionic concentration at the warm electrode (so far as these two factors can be considered apart from one another) we should expect to find the thermo-electromotive force of silver directed in the opposite sense; and also, we should expect to find the electromotive force due to a ratio $C_1 : C_2$ of 1.114 very nearly equal in value to the electromotive force due to a ratio $T_1 : T_2$ of 1.11. The fact that in the latter case the value is five times as great as in the former is highly suggestive that there are other factors entering into the problem besides those of osmotic pressure and solution pressure.

And finally, silver shows an anomalous change of thermo-electromotive force with change of concentration. An increase of concentration in the case of zinc, copper and cadmium gives an increase of electromotive force. In the case of silver, the reverse is true.

## CONCLUSION.

The prime object of the research herein recorded was the collection and coördination of the facts bearing on the thermo-electric behavior of silver, and therefore a record of the investigation practically closes with the statements of the brief summary just given. However, while a discussion of the theories relating to the subject does not properly come within the province of the present paper, yet it will not be out of place to call attention briefly in closing to certain assumptions which suggest themselves as applicable in the explanation of the phenomena observed.

The thermo-electric behavior of silver may be explained for example, in terms of solution pressure and osmotic pressure, on the assumption that the solution pressure of the metal increases, much more rapidly with increase of temperature, than the osmotic pressure of the solution. It must be noted in this connection, however, that it will require a very large increase of solution pressure to account for the outstanding observed electromotive force. It will also be necessary to make the additional assumption that the solution pressure is a function of the concentration, as well as of the temperature. And it must be noted further, that when we have made these assumptions explain the thermo-electric behavior of silver, we meet with serious difficulties in applying the same general explanation to other metals, such as zinc, or cadmium, in which cases the thermo-electromotive force is directed in the opposite sense.

Again, a provisional explanation may be given on the assumption that certain thermo-chemical changes occur in the electrolyte, affecting the degree of dissociation of the salt in solution by the formation of new compounds, as for example, the products of hydrolysis.

In the third place, the phenomena observed with respect to silver may be due to the surface conditions of the electrodes used. For example, if the electrode were covered with a film of oxide, which is assumed to undergo a change more readily on the warm side of the cell than on the cold, there would undoubtedly be established conditions favorable for the production of an electromotive force.

And, to conclude, the peculiar thermo-electric behavior of silver may be explained by applying the assumptions embodied in the Carhart thermo-electric theory of concentration cells — namely, that there is a thermo-electromotive force between a metal and its salt analogous to that between two different metals, and that this thermo-electromotive force is a function of both the temperature and the concentration; and further, that the direction of the thermo-electromotive force, from the metal to the solution or vice versa, depends upon the nature of the metal composing the electrode. The assumptions in this case take no account of forces operating to produce such an electromotive force other than the energy changes which are due to differences of temperature, and which operate in accordance with the laws of thermo-dynamics. These assumptions give an explanation in accordance with the facts; they offer, however, no clue to the mechanism by which the thermo-electromotive force is brought about.

Whatever may prove to be the true explanation of the thermo-electric behavior of silver, certain it is that much remains to be done before very definite statements can be made with reference to this subject or to the more general problem of the relation of heat to electromotive force.

It is planned to continue the present research, dealing with the subject of the thermo-electric behavior of silver over a greater range of temperature than that touched upon in the present case, and also to investigate further the relation of oxidation to thermo-electromotive force.

In conclusion the writer wishes to acknowledge his indebtedness for the loan of a number of important pieces of apparatus by the department of physical chemistry of the University of Michigan, in which department the major portion of the work was done; and to express his appreciation of the interest shown in the work by Prof. H. S. Carhart, of the department of physics, under whose direction the investigation was carried on.

University of Michigan,
Ann Arbor, Mich.,
March 6, 1906.

# INFRA-RED ABSORPTION AND REFLECTION SPECTRA.[1]

By Wm. W. Coblentz.

## Introduction.

MANY chemical compounds contain both oxygen and hydrogen, which, on applying heat, pass off in the form of water. That the water is not united so tenaciously as the other constituents is evident from the fact that in many instances it can be more easily removed; many salts give up their water if exposed to dry air at ordinary temperature. From the circumstance that many of these compounds are crystalline the water is said to be present as *water of crystallization.* The manner in which the water exists in the crystal is not understood. By some it is considered a part of the chemical molecule; by others it is thought that the molecules of water exist in their entirety among the molecules which constitute the crystal. It is characteristic of water of crystallization that it is expelled at a temperature far below red heat, and frequently below 100° C. Another characteristic of minerals containing water of crystallization is their property of reabsorbing water after it has been removed. Copper sulphate is an excellent example; on applying heat, the blue crystal becomes a crumbling white mass, which, if permitted to stand in dry air absorbs water and resumes its blue color and crystalline structure.

On the other hand, the water which is given off only at a red or even a white heat can scarcely be present in the compound in the same manner as the water of crystallization, and is distinguished as *water of constitution.* In this case the water is not supposed to exist as such in the mineral, but to result from the union of oxygen and hydrogen or from the hydroxyl groups contained in the compound.

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[1] Extracts from a memoir submitted to the National Bureau of Standards for publication.

Of course there are minerals which contain water in both these forms. In copper sulphate, $CuSO_4 + 5H_2O$, four molecules of water are given off at 100° and the fifth at 200° so that the latter is possibly combined in some manner different from the former. In epsomite, $MgSO_4 + 7H_2O$, six molecules of water are given off at 132° while the seventh is held more tenaciously and is not given off until heated to 210°.

However, in cases like these, where successive portions of water are given off at different temperatures, it is difficult to draw a distinction between water of crystallization and water of constitution. In the minerals just quoted, however, it has been found that the heat of hydration of the last molecule of water is different from that of the molecules of water which pass off at a lower temperature, which confirms the belief of a difference in the bonding in the two cases.

As a whole, the question of the association of the atoms of oxygen and hydrogen in certain compounds is far from settled, while the difficulties involved in its investigation are very great. The existing data bearing upon the subject is practically *nil.*

## PRESENT METHOD OF INVESTIGATION.

In a preliminary paper bearing upon the question of water of crystallization[1] the writer described the infra-red absorption spectra of two numerals, selenite, $CuSO_4 + 2H_2O$, and brucite, $Mg(OH)_2$, in which the atoms of oxygen and of hydrogen are thought to be combined in a different manner. It was the application of the results of previous work in which it was abundantly proven that certain groups of atoms have characteristic absorption bands. Hence, if the oxygen and hydrogen, which enter into the composition of certain minerals, are bonded as they are in a molecule of water then one would expect to find the absorption spectra of such minerals to be a composite of the bands of ordinary water and of the bands caused by the other constituents.

The only previous investigation bearing on this subject, from the standpoint of infra-red absorption spectra is that of Königsberger,[2] who studied the pleochroism of several minerals including selenite. Unfortunately his plate of selenite was too thick, so that no energy was transmitted beyond 2.5 μ. He calls attention to the fact that a small absorption band at 1.5 μ coincides with that of water, from which it would appear that in selenite the absorption of the water of crystallization does not appear to be different from that of ordinary water.

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[1] PHYSICAL REVIEW, 20, p. 252, 1905.

[2] Königsberger, Ann. der Phys., 61, p. 703, 1897.

Thinking that it would be fairer to select the *large* water bands at 3.0, 4.75 and 6 μ as a criterion, the writer (loc. cit.) examined *thin* sections of several minerals and found as anticipated that minerals containing water of crystallization have large absorption bands coinciding with those of ordinary water. The selection of selinite, $CaSO_4 + 2H_2O$, and brucite, $Mg(OH)_2$, as types of water of crystallization and of constitution was a fortunate one, for two reasons. (1) The selenite curve showed all the absorption bands of water in their proper positions and intensities, except the 4.65 μ band which is shifted and too deep for the thickness of water contained in the plate under examination. The fact that the band is shifted caused me to suspect that it may be complex, and, from the fact that it lies in the region where the NCS-radical and certain sulphur compounds have a strong absorption band, that it may be due to the $SO_4$-radical, a surmise that since then has been unexpectedly verified. (2) Although the brucite curve did not contain the water bands, thus showing the difference between water of constitution and of crystallization, it contradicted my previous work[1] in which it was shown that the OH-radical in the alcohols has an absorption band at 2.95 μ. From the brucite curve the conclusion was drawn that the OH-radical is inactive. Since then I have studied the chemical side of the question more thoroughly from which it appears that there is no marked difference[2] in the activity of the OH-radical in the hydroxide studied, and hence that the brucite curve should have a band at 3.0 μ instead of the one shifted to 2.5 μ. In other words, the present research, which is in part the outcome of the aforesaid discrepancies, has to a very unexpected degree furnished us with an abundance of new proof that certain groups of atoms have definite absorption bands, which really means that these groups of atoms, or "ions" enter into the various compounds in a similar manner.

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[1] Investigations of Infra-red Spectra, Washington, 1905. PHYS. REV., Vol. 22, 1905.

[2] From the chemical standpoint, however, the OH in alcohol and in $H_2SO_4$ is more active, since it is replacable by a metal (more acid) than the OH in brucite $MgO(OH)_2$, which is not replacable (more basic).

To sum up, in the present investigation the criterion for distinguishing water of crystallization from water of constitution, is the presence of absorption bands at 1.5, 2, 3, 4.75 and 6 $\mu$, which is the location of the absorption bands of ordinary water. If there are no other absorption bands nearby then the intensity of these bands should be somewhat like that of ordinary water, viz.: the bands at 1.5, 2, and 4.75 $\mu$ are weak, while the bands at 3 and 6 $\mu$ are very strong.

A hydroxyl group will cause an absorption band at 3 $\mu$. Silicates may have a small band shifting from 2.9 to 3.1 $\mu$, but since it is weak, there is no danger of confusing it with the strong water band in the same region.

## PLEOCHROISM.

Since the present research involves the examination of minerals which are not isotropic, the question presents itself whether it would be better to examine them in natural or polarized light. In the former case we obtain *all* the absorption bands, irrespective of the direction of transmission, but their observed intensities will not necessarily be real. In the latter case where the intensity of the transmitted energy depends upon the direction of vibration of the polarized rays with respect to the axes of the crystal (pleochroism) the observed intensities will be real, the number and position of the absorption bands will depend upon the direction of observation, but the accuracy is less the farther one penetrates the infra-red, due to the loss in the polarizing the source of energy.

By these statements it is not intended to give the impression that pleochroism is not worth considering. The work of Merritt[1] and of Königsberger[2] is especially valuable in demonstrating that absorption is dependent upon the direction of vibration of the incident energy. The visible spectrum is so narrow that it is difficult to separate the absorption bands, while, on the other hand, the infra-red is a vast and almost unexplored region, and it is here that one would expect to resolve wide absorption bands such as exist in the visible spectrum. The curves of Merritt and of Königsberger show this, especially the calcite curves, which are entirely independent for the ordinary and extraordinary rays. Nevertheless, in looking over the previous work it seemed to the writer that in the present state of our knowledge of absorption a greater advance would be made by simply mapping the spectra of a great many minerals for energy transmitted through them in its natural mode of vibration. The results have been most gratifying. If we had been content with the examination of a few, easily obtainable, large-sized crystals like colemanite, for pleochroism, the results would have been quite different.

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[1] Merritt, PHYS. REV., 2, p. 424, 1894.

[2] Königsberger, Ann. der Phys., 61, p. 687, 1897.

The maxima of the absorption of water are constant in position for the amorphous and the crystalline minerals studied, which would indicate that in this case the transmission is not affected by the direction of vibration.

The desirability of examining many minerals is illustrated in the appended curves in which it will be seen that frequently in one region of the spectrum the water bands are obliterated by an increase in the general absorption or by an adjacent absorption band, while in another part of the spectrum the water bands are very distinct.

## APPARATUS AND METHODS.

In the present investigation a mirror spectrometer, a rock slat prism and a Nichols' radiometer were used. Except for certain improvements, the details in mounting and adjusting the different parts have been described elsewhere[1] and it will be sufficient to add that the spectrometer mirrors were 10 cm. in diameter and 50 cm. in focal length, and that the rock salt prism was an unusually fine one, having a refracting angle of 59° 59′ 36″ and faces 9 × 9 cm. area. The spectrometer slits were 0.3 mm. wide, or about 2′ of arc. The time required for the radiometer to reach a maximum deflection was about 20 seconds. The different portions of the spectrum were projected upon the radiometer slit by using the Wadsworth[1] mirror-prism method and rotating the prism table. Although one doubles the error in making spectrometer settings, the method was the most convenient one in the present work. The "heater" of a 110 Nernst lamp, on an 80-volt storage battery circuit was used as a source of energy. The sections were mounted in the usual manner, upon a wooden carrier which moved in vertical ways between the source of energy and the collimeter slit.

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[1] Phys. Rev., Vols. 16 and 17, 1903. Investigations of Infra-red Spectra, Washington, 1905.

To protect the prism from moisture a small crystallizing dish of $P_2O_5$ was placed over it, and when not in use, a large crystallizing dish was inverted over the prism and drying material. The edge of the large dish was ground to fit the prism table, and prevented the entrance of moisture.

## PREPARATION OF THE MINERAL SECTIONS.

Whenever possible the crystals were split parallel to a cleavage plane, since many crystals would break in grinding. The remaining ones were ground thin in the ordinary manner. To accomplish this they were mounted upon glass plates by means of pitch, having a low melting point so as to avoid disturbing the water of crystallization which is expelled from some minerals at a low temperature. The sections were cleaned in chloroform and mounted upon heavy cardboard having rectangular holes about 4 × 10 mm. cut into them. That the crystals were not affected by grinding and the cement was proven in a number of cases where cleavage sections of the same mineral were examined. The sections were entirely free except at the ends which rested upon the cardboard, which was then mounted upon the holder which moved in vertical ways before the spectrometer slit.

In the description of the different minerals, the direction of cutting the sections is parallel ($\| a$) to some crystallographic axis. In many crystals there is usually a perfect cleavage parallel to one of the crpstallographic axes, which fact was taken advantage of in preparing the sections. The cleaving was done by means of a small knife-blade struck with a light piece of metal, for example, a file.

In the present research the examination of the sections after being prepared was overshadowed by the difficulty in obtaining specimens of sufficient size and in grinding them thin enough. In my previous work it was found that as a general rule the compounds examined increase in their general absorption beyond 5 $\mu$, so that the (liquid) films had to be reduced to 0.01 mm. In the present work it was impossible to reduce the thickness to much less than 0.1 mm. with the consequent result that many sections became opaque beyond 5 $\mu$.

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[1] Wadsworth, Phil. Mag. (5), 38, p. 346, 1894.

The minerals were obtained from various dealers and from the U. S. National Museum. They were selected according to composition. Of the total number thus selected only about 40 per cent. were obtainable and these were oftentimes the least desirable to illustrate the points in question. The expense involved is no small item, and I am very grateful to the Director for his generosity in meeting that question.

## Scope of Present Investigation.

The principal object in this research was to gain information in regard to the molecular structure of minerals containing oxygen and hydrogen. To this end minerals were selected containing these constituents. Previous work has shown that in organic compounds certain radicals have characteristic absorption bands. One would therefore naturally expect to find similar relations in inorganic compounds, where more important radicals are to be found. Hence, the list was extended, so as to contain a series of minerals having the radicals $CO_2$, $PO_4$, $SO_4$ and OH. The results obtained serve the purpose very well for demonstrating the rashness to attempt to establish "laws" from present data for future investigators to refute, just as is being done at present in more thoroughly explored fields, such as for example the absorption of solids in solution.

In the study of the carbon compounds in inorganic chemistry, their constitution has been established by the replacement of certain constituents by organic radicals, by the preparation of a series of derivatives, by vapor density determinations or by studying their physical properties in solution. Mineralogy is essentially the chemistry of silicon compounds, to which, as yet, it has not been possible to apply any of the above methods, so that the constitution of many minerals has been derived from analogies with other compounds which are better understood. Hence, in an investigation like the present it is not surprising to find exceptions to the tentative rules for classifying these minerals.

The transmission curves are given without correction for reflection on the surfaces. In most cases, as will be noticed from the reflection curves, the correction is negligible. One case, viz., stibnite, $Sb_2S_3$, such a correction is worthy of notice. The transmission shows a uniform value of 45 per cent. To the writer this seemed a very transparent substance until the greater surprise of a uniform reflecting power of about 43 per cent. was observed, which indicates that after correcting for reflection this mineral (for the thickness examined) is practically transparent.

## Absorption Spectra of Different Minerals.

### *Group I., Minerals Containing Water of Crystallization.*

Under this heading are to be found all the minerals studied which are generally thought to contain water of crystallization. First of all it will be necessary to consider the absorption spectrum of water which has been studied by Julius,[1] Paschen,[2] Aschkinass[3] and

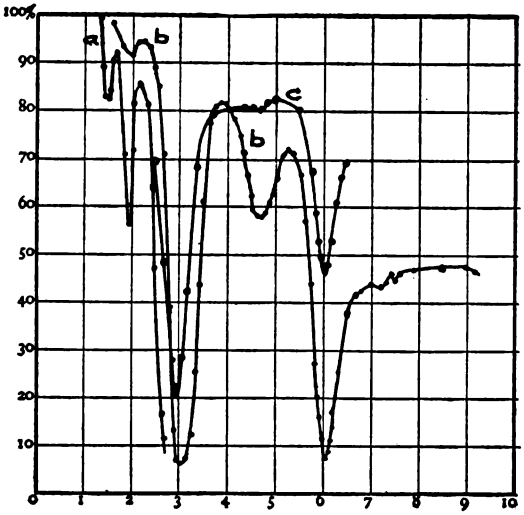

Fig. 1. Water.

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[1] Julius, Verhandl. Kōnigl. Akad. Amsterdam, Deel I., No. 1, 1892.

[2] Paschen, Ann. der Phys. (3), 53, p. 334, 1894.

[3] Aschkinass, Ann. der Phys. (3), 55, p. 406, 1895.

others. All observers agree in their location of large absorption bands at the approximate wave-lengths 1.5, 3, 4.75 and 6 $\mu$.

All have found water extremely opaque to infra-red radiation, so that the film had to be reduced to a few thousandths of a millimeter in order to be able to study it at all. In Fig. 1 are given the absorption curves (*a* and *b*) of water as found by Aschkinass. His values of the maxima are slightly greater than those found by others, but this is simply due to a fault in his calibration. The curves for the different thicknesses ($a = .05$, $b = .01$ mm.) illustrate very well what we are to expect in the case of minerals containing several molecules of crystal water. For a very much thinner film (curve $c = .001$ mm.) examined by the writer[1] the absorption band at 4.75 $\mu$ has entirely disappeared.

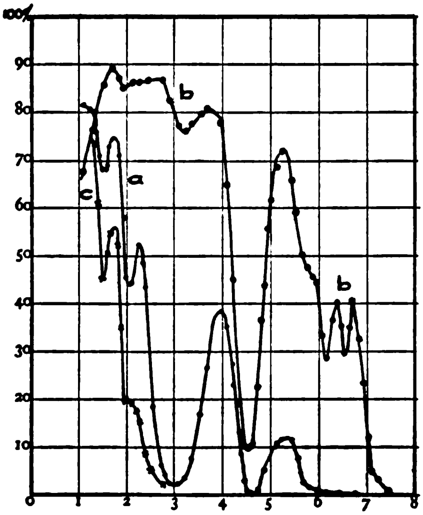

Fig. 2. $a$ = Selenite, $t$ = 0.648 mm., $b$ = Anhydrite, $t$ = 0.656 mm., $c$ = Selenite, $t$ = 2.57 mm.

SELENITE, $CuSO_4 + 2H_2O$.

ANHYDRITE, $CaSO_4$.

(Figs. 2 and 3; selenite monoclinic, cleavage || *b*, $t = .648$ mm. Anhydrite, orthorhombic cleavage piece || *c*, $t = .656$ mm., from Stassfurt, Germany.)

Of all the minerals studied containing water of crystallization these two are the most conspicuous for demonstrating the effect of the presence of $H_2O$. It would have been highly desirable to procure more minerals which occur in the hydrous and anhydrous state, but none were obtainable. The artificially dehydrated minerals, such as copper sulphate, were too opaque for examination after expelling all the water. The only exception is selenite, the various curves of which will now be considered. The anhydrite curve, *b*, is to be noticed first, from which it will be observed that there are small bands at 1.9, 3.2, 5.7, 6.15 and 6.55 $\mu$ and an enormous band at 4.55 $\mu$, which will be shown later to be due to the $SO_4$ ion.

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[1] PHYS. REV., 20, p. 257, 1905.

Turning to the selenite curve, *a*, Fig. 2, it will be noticed that it is less transparent for the same thickness, 0.65 mm., and that in its general trend it is similar to the curve for water. All of its absorption bands coincide with water, with the exception of the 4.75 $\mu$, as was found on examining the anhydrite. The band 3 $\mu$ is widened by the presence of the anhydrite band at 3.2 $\mu$. The curve *c* for a thickness of 2.57 mm. is due to Königsberger (loc. cit.).

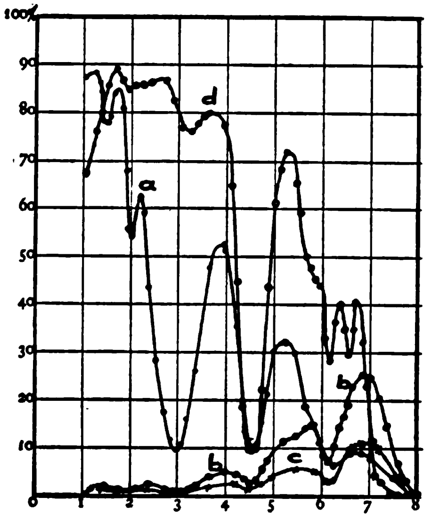

Fig. 3. *a*, *b*, *c*, = Selenite, $t = 0.204$ mm. *d* = Anhydrite, $t = 0.656$ mm.

In Fig. 3 is illustrated the effect of dehydrating the selenite. This was accomplished with difficulty on account of the warping and shrinking of the plate, which necessitated the dismounting of the specimen for each heating. It was found necessary to clamp the specimen between two metal plates in order to prevent it from warping and breaking. Curve *a* gives the clear piece having a thickness of 0.204 mm. Curve *b* shows the transmission after partial dehydration. It is of considerable interest in showing the permanence of the 4.55 μ band. Beyond 6 μ the transparency increases and becomes 1.5 times as great as selenite at 6.9 μ. The dehydrated section, which is an opaque white mass, was then moistened with water and allowed to stand over night to dry and set, just as in the case of plaster of paris. The result is shown in curve *c*, where the transparency at 6.9 μ has decreased to almost the original value found for the transparent crystal. It will of course be understood that the great opacity up to 5 μ for the dehydrated section is due to the lack of homogeneity introduced in expelling the water, which has the well known property of scattering the radiation of short wave-lengths. At 7 μ the increase in absorption due to the presence of water cannot be doubted.

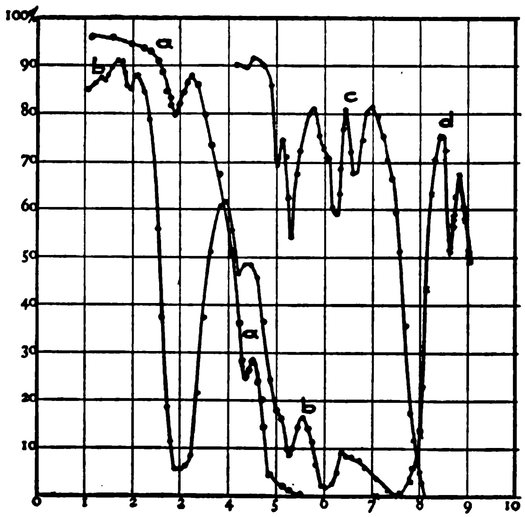

Fig. 4. *a*, *c*, *d*, = Quartz ; *b* = Opal.

QUARTZ, $SiO_2 = SiO_2$.
OPAL, $SiO_2 + xH_2O$.

(Quartz cut axis. $t = 1.30$ mm. Opal, massive, transparent. $t = 0.12$ mm.; Fig. 4.)

The specimen of quartz examined was made for polariscopic work and was perfectly clear. Its transmission curve, *a*, Fig. 4, shows small bands at 2.9 $\mu$ and 4.35 $\mu$. Curve *c*, which shows a series of bands at 5.02, 5.3, 6, 6.26 and 6.65 $\mu$, is due to Nichols[1] who used a section 0.018 mm. thick. Unfortunately his curve begins in the slight band at 4.35 $\mu$ so that there is no check upon its accuracy of location.

Königsberger[2] examined smoky quartz and found bands at 3.05 and 4.05 $\mu$. Merritt[3] using polarized light found bands at 3 and 3.6 $\mu$ for the extraordinary ray, and bands at 2.9, 3.75 and 4.1 $\mu$ for the ordinary ray.

For amethyst, which is violet quartz, of which the color has been attributed to manganese, Königsberger found an absorption band at 3.1 $\mu$. As a whole different observers agree in locating a small band near 3 $\mu$ which will not interfere in considering water of crystallization.

Opal is quartz containing variable proportions of water, from 5 to 30 per cent. It shows no traces of crystallization. Neither is it considered a solid solution, for the water contained is not a function of the vapor pressure. The transmission curve of opal has the general outline of the curve for water and contains the bands of water at 1.5, 2, 3 and 6 $\mu$, as well as the silicon bands at 4.2 and 5 $\mu$. The 3 and 6 $\mu$ bands are the composite of the water and silicon bands in those regions.

### HEULANDITE, $H_4CaAl_2Si_6O_{18} + 3H_2O$.

(Section ground || *b*. $t = 0.20$ and 0.22 mm., semitransparent. Fig. 5).

Heulandite belongs to a class of minerals called zeolites[4] which are hydrated silicates of alumina, alkalies and generally lime. To this class belong heulandite, stilbite, analcite, natrolite and scolecite, which are included in the present research.

In these minerals the water of crystallization is very loosely held. It is impossible to distinguish between water of constitution and water of crystallization. The water continues to be gradually expelled as the temperature is raised and may be replaced by other substances such as $NH_3H_2S$ or $C_2H_5OH$. The dehydrated crystals absorb definite quantities of these substances, as a sponge absorbs water, the process being accompanied by the evolution of heat.

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[1] Nichols, PHYS. REV., 4, p. 297, 1896.

[2] Königsberger, Ann. der Phys. (3), 61, p. 687, 1897.

[3] Merritt, Ann. der Phys. (3), 55, p. 49, 1895.

[4] Miers, Mineralogy, p. 483.

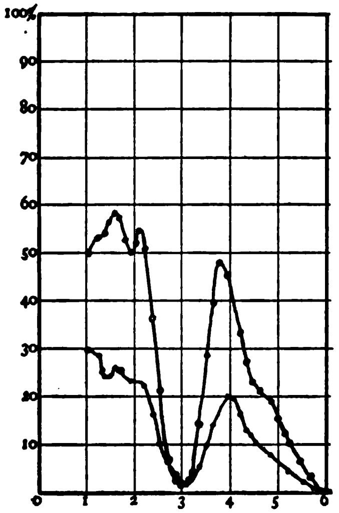

Fig. 5. Heulandite.

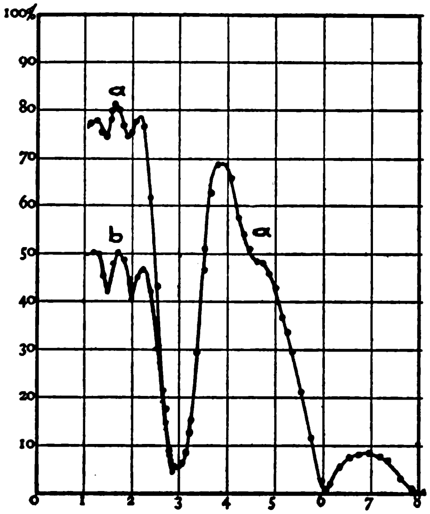

Fig. 6. Stilbite (*a*) and Potassium Alum.

Since the per cent. of water present varies continuously with the vapor pressure it is generally concluded that the water of the zeolites is not analogous to the water of crystallization of most hydrated salts, but resembles more nearly the intermixture which occurs in solid solutions.

In Fig. 5 two curves of heulandite are given. The sections were about the same thickness and the great difference in transparency is due to the fact that the crystals were of different homogeneity and transparency. The curves show the presence of the water bands at 1.5, 2, 3 and 4.75 $\mu$ beyond which point the opacity becomes too great for further exploration.

The crystals obtainable were small, so that the section was not quite long enough to cover the whole slit.

STILBITE, $CaAl_2Si_6O_{16} + 6H_2O$.

(Transparent section cut $\perp$ to optic axis. $t = 0.11$; curve *a*, Fig. 6.)

The stilbite curve is to be noticed for its great transparency with all the water bands superposed. There do not appear to be any important bands belonging to the mineral itself.

POTASSIUM ALUM, $K_2SO_4Al_2(SO_4)_3 + 24H_2O$.

(Cut ⊥ axis. $t = .085$ mm., transparent; curve *b*, Fig. 6.)

The exploration of the spectrum extends only to 3 $\mu$. The water bands at 1.5 and 2 $\mu$ are present. With 24 molecules of water and $SO_4$ bands at 4.55 $\mu$, to be mentioned later, it would not be possible to penetrate beyond 3 $\mu$, unless a thinner section could be made.

NATROLITE, $Na_2Al_2Si_3O_3O_{10} + 2H_2O$.

(Orthorhombic section ground ‖ *m*, subtranslucent. $t = 0.11$ mm.; curve *a*, Fig. 7.)

The specimen from which this section was cut was a tuft of acicular crystals. The section was made from the more massive part, and was almost opaque for the thickness used. The curve *a*, in Fig. 8, shows the water bands in their usual positions and proper intensities.

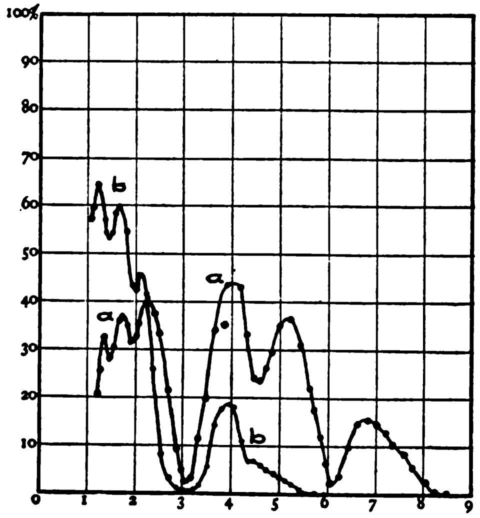

Fig. 7. Natrolite (*a*) and Scolecite.

SCOLECITE, $CaAl_2Si_3O_{10} + 3H_2O$.

(Monoclinic, section split ‖ *m*, perfectly transparent. $t = 0.565$ mm.; curve *b*, Fig. 7.)

This mineral differs from the preceding in being a lime zeolite, and having one more molecule of water. Its greater homogeneity makes it more transparent in the region of the short wave-lengths. It has the general outline and the absorption bands of water up to 5 $\mu$ where it is completely opaque. The 3 $\mu$ band is evidently complex. Professor S. L. Penfield kindly presented this specimen.

CALCIUM CHLORIDE, $CaCl_2 + 6H_2O$.

(Film melted between rock salt. $t = 0.1$ mm., Fig. 8.)

This compound comes in large hexagonal crystals. A specimen was melted between two plates of rock salt, and stood over $P_2O_5$ for several days, until the edges became white from dehydration. The substance recrystallized in the meantime, and when examined showed the water bands in their usual position and intensities, except the 3 $\mu$ band which is shifted to 3.2 $\mu$.

POTASSIUM FERROCYANIDE, $K_4Fe(CN)_6 + 3H_2O$.

(Section split || $c$, transparent. $t = 0.3$ mm.; curve $b$, Fig. 8.)

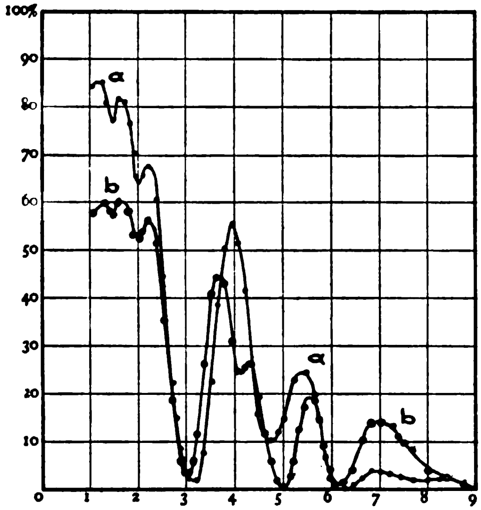

Fig. 8.

The water is so easily expelled from this mineral that the heater had to be used on 70 volts. The transmission curves show the water bands at 1.5, 2 and 3 $\mu$, while the next two bands are shifted to 5 and 6.2 μ respectively. Porter[1] by means of "reststrahlen" located a band at 4.84 μ.

**Mellite**, $Al_2C_{12}O_{12} + 18H_2O$ (Fig. 9).

This mineral occurs as waxy crystals of variable transparency in European coal measures. It was selected on account of its carbon, and also because of the large number of molecules of water, which is expelled at a low temperature.

In Fig. 9 curve *a* is given the transmission curve of a mineral from Steeg & Reuter, purporting to be mellite or "honeystone," *t* = .125 mm. It was the most flagrant exception of the rule that minerals having water of crystallization are very opaque and have absorption bands in common with water. Evidently this needed further investigation; and this was done with minerals purchased from various dealers, care being taken to obtain them from different localities. Curves *b* and *c* give the transmission for transparent yellow crystals, *t* = 0.7 and 0.15 mm., respectively, which came from Arten, Thuringia. Curve *d* is the transmission for a grayish white transluscent crystal, ground to 0.12 mm. in thickness, from Mallonka, Austria. Curve *e* is for a white transparent crystal, 0.06

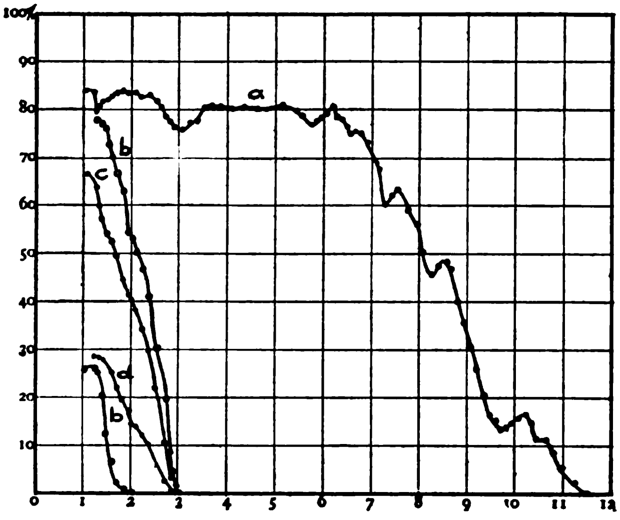

Fig. 9.

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[1] Porter, Ap. Jr., 22, p. 229, 1906.

mm. in thickness, from Tula, Russia. In all these curves it will be noticed there is no energy transmitted beyond 3 $\mu$, while from the very nature of the transmission curves the 1.5 band is invisible, while the 2 $\mu$ band is almost obliterated. As a whole the theory that in crystal water the bonding is the same as in ordinary water has also been confirmed with mellite. A letter of inquiry to Steeg & Reuter in regard to the sample sent us revealed the fact that cassiterite, $SnO_2$, was accidentally substituted for mellite. The fact that it was possible to detect the error would indicate that the method of analysis is trustworthy, and in that respect it is fortunate that the substitution occurred.

About twenty other substances were examined which contain water of crystallization and they all show the bands of ordinary water. The list includes a number of sugars, nearly all of which contain water of crystallization. One of these sugars, *d*-fructose, $C_6H_{12}O_6$, does *not* show water bands, as was to be expected. Cane sugar, $C_{12}H_{22}O_{11}$, whether in a melted condition or a crystal, "rock candy," *shows water bands.* An analysis showed that the water content was about 0.05 per cent., which is too small an amount to account for the bands. Now, it has never before been suspected that cane sugar has water of crystallization and the present disagreement with the results of chemists who have made a life-long study of sugars in general must be considered with caution. A comparison with lactose, maltose and dextrose would indicate the presence of a molecule of water in crystallization.

Sugars are rich in OH groups, which with the $CH_3$ will confuse matters at 3 to 3.5 $\mu$, so that the effect of water must be based upon the small bands at 1.5 and 4.75 $\mu$. As a whole, the question is obviously in an unsettled state, with the present data indicating the presence of a molecule of water of crystallization in cane sugar which has heretofore been considered to be composed entirely of water of constitution.

### *Group II., Minerals Containing Water of Constitution.*

The first part of this group contains minerals in which the oxygen and hydrogen are present in the form of the univalent hydroxyl radical, OH, and which are known as hydroxides. The hydroxides when heated also yield water, but it is a characteristic that they must be strongly heated before they are decomposed. From previous work, already noticed we would expect an absorption band at 3 $\mu$ for hydroxides.

Manganite, MnO(OH).

(Orthorhombic, ground $\|$ $m$ opaque, $t = 0.08$ mm., Fig. 10.)

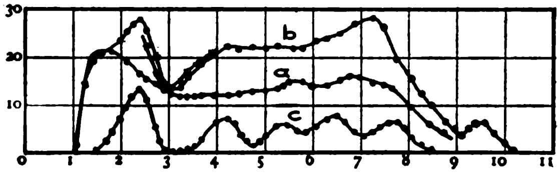

Fig. 10.

As will be noticed in curve *a* of Fig. 10, manganite has no sharp bands throughout the whole region to 9 $\mu$. There is a slight indication of a band at 3 $\mu$, and another at 6.2 $\mu$.

Gothite, FeO(OH).

(Section ground $\|$ $b$, $t = 0.15$ mm., curve *b*, Fig. 10.)

The appearance of this mineral is opaque, black metallic luster, and as a whole would not impress one as being quite transparent to 9 $\mu$. It transmits about 20 per cent. of energy throughout this whole region, which is in marked contrast with the almost complete opacity of iron. The 3 $\mu$ band is well-marked while a second one occurs at 9 $\mu$. This specimen was kindly presented by Professor S. L. Penfield.

Bauxite, $Al_2O(OH)_4$.

(Chocolate-brown color. $t = 0.11$ mm., curve *c*, Fig. 10.)

In this mineral the 3 $\mu$ band is wide and complex. There are other bands at 4.7, 5.8 and 7 $\mu$.

Turquoise, $AlPO_4$. $Al(OH)_3 + H_2O$.

(Massive light-green. Subtransparent in section of 0.1 mm., curve *a*, Fig. 27).

This mineral is supposed to contain a molecule of water, although Miers writes the formula without it. The OH groups will cause a band at 3 $\mu$ and in general the substance is very opaque so that it is difficult to decide that question. The region at 3 $\mu$ is complex with the maximum at 3.3. There are other bands at 5.1, 5.3, 5.6, 6.3 and 7.6 μ, all of which are small. There seem to be no bands belonging to $PO_4$.

**Lazulite**, $(Mg.Fe)Al_2(OH)_2(PO_4)_2$.

(Massive blue by transmission. *t* = 0.19 mm., curve *b*, Fig. 27.)

The 3 μ band is prominent, while a new band appears at 4.3 μ.

**Hydrargillite**, $Al(OH)_3$.

(Stalactitic mass, *t* = .02 mm., subtransparent, curve *a*, Fig. 11.)

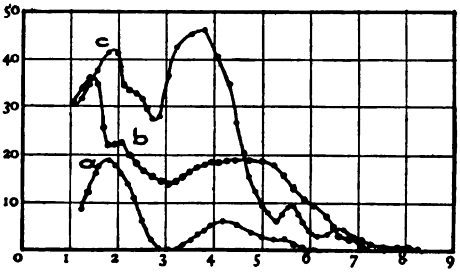

Fig. 11.

The section obtainable was only about 6 mm. long, which did not cover the entire slit, hence the opacity is not quite so great as it appears. There is only one large band, at 3 μ, which is no doubt due to the OH radicals.

**Diaspore**, $AlO(OH)$.

(Cleavage piece ‖ *b*. *t* = 0.18, curve *b*, Fig. 11.)

The specimen was transparent with a few particles that were translucent. The specimen came from Professor Penfield. The band at 3 μ is wider, not so well defined as in the preceding. There are smaller absorption bands at 1.9, 5.8 and 6.7 μ.

**Datolite**, $Ca(BOH)SiO_4$.

(Section ground to 0.23 mm., curve *c*, Fig. 11.)

In the curve the OH band at 3 μ is shifted to 2.8 μ. The other bands present are at 2.3, 5.3 and 6.3 μ. Although the specimen was full of cracks it is rather transparent for a boro-silicate.

**Azurite**, $2CuCO_3.Cu(OH)_2$.

(Translucent section ‖ *c*. *t* = 0.35 mm. thick, curve *c*, Fig. 12.)

The section was ground from a group of crystals all of which were apparently ‖ *c*. There are absorption bands at 2.5, 3.05, 3.58

and 4.05 $\mu$ and complete opacity beyond 5.5 $\mu$. The 3.05 $\mu$ band is shifted slightly from the position common to substances containing OH groups.

**Brucite**, $Mg(OH)_2$.

(From Woods' Mine, Lancaster Co., Pa. Foliated, massive, lamina || *c*. $t = .05$ and $t = 0.19$ mm., Fig. 12.)

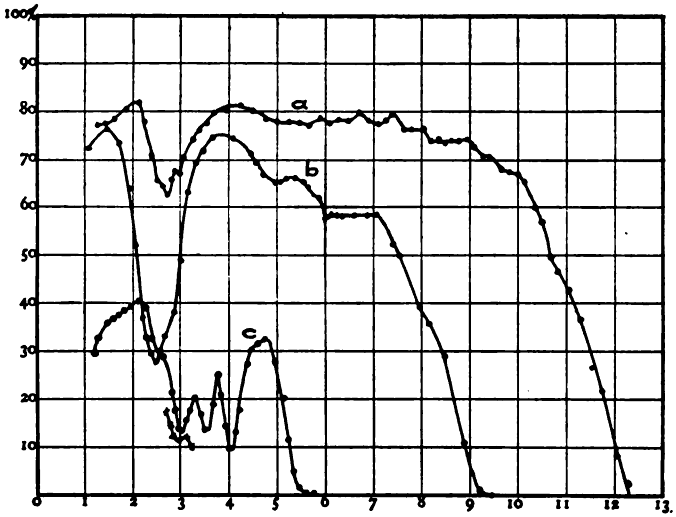

Fig. 12.

As mentioned elsewhere, the fact that brucite did not show an absorption band at 3 $\mu$, which is the maximum of the hydroxyl group in a series of organic compounds previously studied, made a reëxamination highly desirable. Of course, as will be noticed in curve *b*, by straining matters one might have concluded that the band at 2.5 $\mu$, which evidently is complex, contains the 3 $\mu$ band. In the present examination the cleavage section was perfectly transparent and much thinner than the previous one. Furthermore the dispersion is greater, so that as a whole this large band is resolved into three components with maxima at 2.5, 2.7 and 3 $\mu$. Beyond this region these are no marked bands, while beyond 12 $\mu$ there is complete opacity. The curves show depressions at 5, 7, 7.7, 8.2, 9.7 and 10.8 $\mu$, but as a whole the curve is conspicuous for the complete absence of sharp absorption bands, except at 2.7 $\mu$, which is similar to glass and the micas.

PORTLAND CEMENT.

($t = 0.17$ mm.)

The specimen examined was ground thin from a piece made for tensile strength tests. It is known as the "Atlas Brand" and in making it was mixed with 21 per cent. of water. The chemical constitution of Portland cement is unknown. According to le Chatlier[1] the action of water causes the formation of a hydrous silicate $(SiO_2.CaO.).5H_2O$ and a hydrous aluminate $Al_2O_34CaO.12H_2O$.

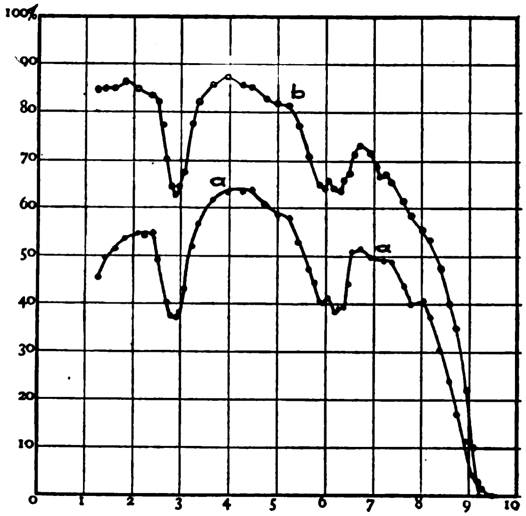

Fig. 13.

From the present curve it will be noticed that the substance is very opaque, with a large absorption band at 3 $\mu$, which would seem to indicate hydroxyl groups. From the curves of mellite and alum it appears that Portland cement is too transparent to contain the number of molecules of water indicated by le Chatlier.

CHLORITOID, $H2(Mg.Fe.)Al_2SiO_7$.

(Variety masonite, cleavage piece || *c*, transmits blue-green. $t = 0.25$ mm.)

This mineral is very opaque to infra-red radiation. There are several small absorption bands, viz.: at 2.3, 2.6, 3.3, 5.6 and 6.3 $\mu$.

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[1] Le Chatlier, Annales des Mines, February, 1888.

As in the preceding, the point of interest is the absence of bands at 1.5 and 3 $\mu$.

CLINOCHLORE, $H_8Mg_5Al_2Si_3O_{18}$.
PENINITE, $H_8(Mg, Fe)_5Al_2Si_3O_{18}$.

(Clinochlore, $t = .08$ mm. Peninite, curve *b*, $t = .04$ mm., Fig. 13.)

These two minerals belong to the chlorite group, which is related to the micas, to be noticed presently. These minerals contain about 12 per cent. of water, which is given off at a high temperature.

Their transmission curves are usually similar to those of the micas. There are absorption bands at 2.9, 5.9, 6.3, 7.1 and 7.8 $\mu$. The frequently recurring bands at 2.9 and 5.9 $\mu$ with the metallic reflection band at 8.5 and 9.02 $\mu$ reminds one of a harmonic series. It may be that these bands belong to a slowly converging spectral series, if not a harmonic series; for the first band oscillates between the values 2.8 and 2.95 $\mu$, while the next band shifts from 5.6 to 5.9 $\mu$, as will be noticed in the micas. As already mentioned the constitution of many minerals is still doubtful. Clinochlore is one of these. From analyses made by Clarke and Schneider[1] it was inferred that the hydroxyl groups MgOH and $Al(OH)_2$ are present. In the present examination there is no indication of a band at 3 $\mu$, which is a characteristic of the OH radical.

TOURMALINE, $H_6Na_2Fe_4B_6Al_3Si_{12}O_{63}$.

(Cut || optic axis.)

These curves are due to Merritt (loc. cit.) and show the variation in transmission for the ordinary ray (plotted ——) for the extraordinary ray (——) and for the unpolarized light. The important absorption bands are at 1.28 and 2.82 $\mu$. The latter is to be noticed in considering the effect of $SiO_2$, $SiO_3$ and $SiO_4$ groups.

$$\text{MICAS}\begin{cases}\textit{Muscovite},\ H_2KAl_3(SiO_4)_3.\\ \textit{Biotite},\ (H, K)_2(Mg, Fe)_2Al_2(SiO_4)_3.\end{cases}$$

(Cleavage || *c*; curve $a =$ muscovite, $t = 0.02$ and .04 mm.; curve $b =$ biotite, $t = .03$ mm., Fig. 14.)

The constitution of the micas is involved in a greater or less degree of uncertainty. They are all silicates of aluminum and

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[1] Clarke and Schneider, Amer. Jour. Sci., 40, 405, 1870.

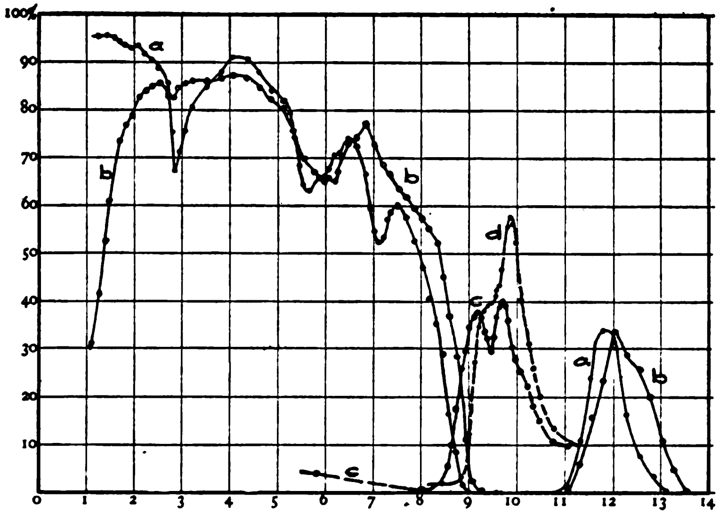

Fig. 14.

either K, Ba, Li or of Fe and Mg. All the micas yield water upon ignition, but it is uncertain whether this water of constitution is due to the presence of H or OH. There is no deep wide absorption band at 3 $\mu$, so that judging by the present method of examination, there cannot be any hydroxyl groups present. Muscovite has a deep narrow band at 2.85 $\mu$ and smaller bands at 1.9, 3.6, 5.6, 5.9, 6.3 and 7.1 $\mu$. Biotite has small bands at 2.8, 5.9, 6.2 and 6.7 $\mu$, and indications of bands at 5.6 and 7 to 8 $\mu$. It has also a band in the visible spectrum. Curves *c* and *d* are reflection.

Both micas have a large opaque region at 9 to 11 $\mu$ followed by a transparent region at 12 $\mu$, beyond which there is again complete opacity. Rubens and Nichols[1] have found metallic reflection bands at 8.32, 9.38, 18.40 and 21.25 $\mu$. It will thus be noticed that the bands located by the writer, by reflection and by transmission do not coincide, as is to be expected in a region of anomalous dispersion.

TALC, $H_2Mg_3Si_4O_{12}$.

(Subtransparent, $t = .06$ mm., curve *c*, Fig. 15.)

In talc water is expelled at red heat. From its stability with acids it is considered an acid metasilicate. From analyses of Clarke and Schneider (loc. cit.) no hydroxyl groups were inferred, and the transmission curve does not show a band at 3 μ. Talc has absorption bands at 5.6, 5.95 and 7.15 μ.

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[1] Rubens and Nichols, Ann. der Phys. (3), 60, p. 418, 1897.

Serpentine, $H_4(MgFe)_3SiO_9$.

(Massive, subtranslucent, curve *a*, $t = .225$ mm., $b = 0.08$ mm. From Montville, N. J., Fig. 15.)

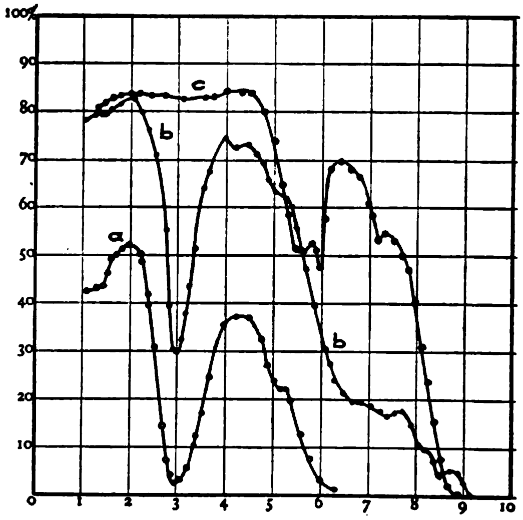

Fig. 15.

In serpentine the water is chiefly expelled at red heat. According to Miers[1] both talc and serpentine are to be regarded as basic and not hydrated silicates, since they part with their water only at a high temperature. From the curves of serpentine which show a large absorption band at 3 μ, if the results from the present method of examination are to be trusted, it would appear that there are hydroxyl groups present. From the analyses of Clarke and Schneider[2] it was inferred that the Mg is present as MgOH and hence the formula is written $H_3(MgOH)Mg_2(SiO_4)_2$. It has also been written with two magnesium hydroxyl groups. Serpentine has absorption bands at 1.4, 3, 5, 6.6, 7.4, 8.1 and 8.5 μ.

### *Group III., Miscellaneous Compounds; Sulphates.*

It has been noticed elsewhere that in the examination of selenite the large absorption band at 4.55 μ is shifted and too deep to belong to water; also that it was suspected to be due to the $SO_4$ groups of atoms. The band has further been noticed in discussing selenite and anhydrite, Fig. 3, and in thaumasite and blödite. Under the present heading will be discussed the absorption spectra of simple sulphates formed by the combination of a metallic oxide and sulphur trioxide, all of which show a band at 4.55 $\mu$, while several have ahother band in common at 6.5 $\mu$.

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[1] Miers, Mineralogy, p. 439.

[2] Clarke and Schneider, Amer. Jour. Sci., 40, p. 308, 1890.

BARITE, $BaSO_4$.

(Orthorhombic, section || *c*, translucent, $t = 0.25$, curve *a*, Fig. 16, from Cheshire, Conn.)

The barite curve is quite opaque due in part to numerous cracks. There are bands at 3, 4.6, 6.2, 6.5 $\mu$. Königsberger's curves show that the band at 4.6 $\mu$ is wide and shifts for different directions of vibration of polarized light.

GLAUBERITE, $Na_2So_3CaSO_4$.

(Monoclinic, cleavage section || *c*, transparent, $t = 1.26$ mm., curve *b*, Fig. 16.)

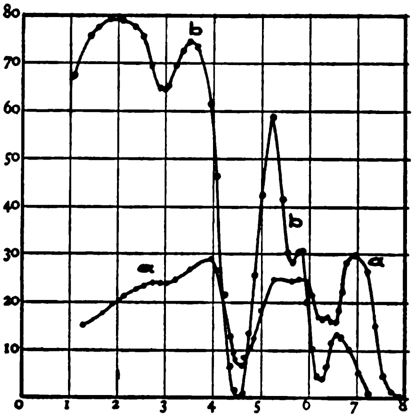

Fig. 16.

This is a mixture of two sulphates of which the $CaSO_4$ bands at 3.2 and 4.55 $\mu$ have already been noticed. Glauberite has bands at 3, 4.55, 5.6 and 6.2 $\mu$.

THENARDITE, $Na_2SO_4$.

(Borax Lake, Calif. Orthorhombic, ground || *c*, 2.2 mm.)

This material was too brittle to grind successfully. It shows a large band at 3.1 and 4.55 $\mu$.

Kieserite, $MgSO_4$.

(Stassfurt Mines. Massive, subtranslucent. $t = 0.22$ mm.)

This mineral, like selenite, shows both water and $SO_4$ bands. It is very opaque. The water bands at 1.5, 3, 4.55 (complex with $SO_4$) and 6.05 $\mu$. There are two small bands at 1.8 and 7 $\mu$, respectively.

Celestite, $SiSO_4$.

(Lampasao, Texas. Cleavage $\parallel c$, transparent. $t = 0.67$ mm.; curve *a*, Fig. 17.)

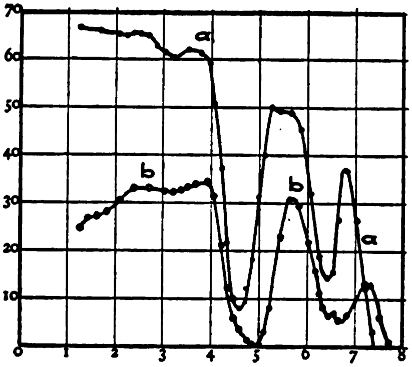

Fig. 17.

Celestite has absorption bands at 3.2, 4.55 and 6.4 $\mu$. The 4.55 band is conspicuous for its great depth.

Anglesite, $PbSO_4$.

(Monte Poni, Sardinia; translucent, section $\parallel$ m. $t = 0.7$ mm.; curve *b*, Fig. 17.)

The section used was not quite long enough to cover the slit. The lack of transparency was in part due to the fact that on account of its brittleness the section was not highly polished. The band at 4.55 $\mu$ is complex, with a deeper one at 5 $\mu$. The same is true of the 6.4 $\mu$ band, which is complex with a stronger band at 6.7 $\mu$. There are slight depressions at 1.9 and 3.2 $\mu$.

The examination includes various other compounds which would be too extensive to enumerate. At least 110 were examined, and the spectrum of each mineral forms an interesting study by itself.

Part IV. consists of an investigation of reflection spectra of the aforesaid minerals which were of sufficient size to permit an examination. The silicates, *e. g.*, the feldspars and micas, show a region of selective reflection from 8 to 10 $\mu$, some of the bands of which evidently are due to $SiO_2$. The sulphates have a region of selective reflection at 8.5 to 9.1 $\mu$, the latter band being harmonic with the one at 4.55 $\mu$.

The reflecting power of the sulphides of ZnFe and Sb are worthy of notice. They are known for their metallic lustre, especially Stibnite, $Sb_2S_3$. Their reflecting power in the infra-red is equally conspicuous for its high value, which is uniform throughout the region examined to 12 $\mu$. Stibnite is the most marked in this respect. By transmission it was found to be unusually transparent, the absorption of a thin film, 0.4 mm., being about 44 per cent. throughout the whole region to 12 $\mu$. The reflecting power was found to be about 43 per cent., so that the true absorption for this thickness is only some 2 or 3 per cent., which has been found in but few substances except gases.

The results obtained from the present examination of reflection spectra demonstrate a number of important facts. The first one is the dependence of reflection upon absorption. The second point worthy of notice is that region of selective reflection begins beyond 7 $\mu$ while for the majority of substances studied, the region of greatest activity is from 8 to 10 $\mu$. Whether this coincidence in the grouping of reflection bands (of minerals other than those containing $SiO_2$) is fortuitous is unknown. A knowledge of their dielectric constants might aid in deciding this point. In considering this question of the selective reflection beyond 7 $\mu$ it will be recalled that the "general absorption" of many substances was found[1] to increase beyond this point.

The results as a whole show that in the silicates there are not such definite bands, whether found by reflection or by absorption, as one would expect. In other words, the silicon radical seems to be differently bonded in each mineral. Possibly there are several radicals $SiO_2$, $SiO_3$, $SiO_4$, one or more of which are present in each mineral, or even in different specimens of the same mineral. This would explain the lack of constancy of the occurrence oft he bands of quartz of 3 $\mu$.

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[1] "Investigations of Infra-red Spectra," Washington, 1905.

The investigation has added one more radical which has definite absorption bands in the infra-red, *viz.*, $SO_4$, which has harmonic bands at 4.55 and 9.1 $\mu$.

## SUMMARY.

The transmission and reflection spectra of at least 120 compounds have been examined, many of them to 15 $\mu$, by means of a mirror spectrometer, a rock-salt prism and a Nichols radiometer. The aim of investigation was the study of a series of minerals containing oxygen and hydrogen in the form of what is known as water of constitution and water of crystallization. The interpretation of the results are based upon the assumption that if the bonding of the oxygen and the hydrogen in the molecules is similar to that in ordinary water, then the absorption spectra of minerals containing these two elements thus bonded should show the absorption bands of water superposed upon the absorption spectrum of the other constituents.

On the other hand minerals containing oxygen and hydrogen as water of constitution should not show the water bands except hydroxyls which should show a band at 3 $\mu$.

The results show that of some 30 minerals containing "water of crystallization" there are no important exceptions to the rule that they should show the bands of ordinary water. On the other hand the one important exception to the rule that minerals containing "water of constitution" should not show water bands is cane sugar. Minerals containing hydroxyl groups generally have a marked band at 3 $\mu$. Sulphates have a strong band at 4.55 $\mu$, and a less constantly recurring band at 9.1 $\mu$, due to the $SO_4$ ion. On the other hand the silicates do not have such definite bands which would seem to indicate that the bonding of the silicate radical is different in each mineral containing that element. The examination includes minerals of which the chemical constitution is in doubt, for example, talc and serpentine. The former is not supposed to contain hydroxyl groups, while in the latter such groups are inferred. The present examination supports these views in that the transmission curve of talc does not contain an absorption band at 3 $\mu$, while serpentine contains a large band at 3 $\mu$, which is in common with substances containing hydroxyl groups.

WASHINGTON, D. C.,
May 28, 1906.

# THE COTEMPORANEOUS VARIATIONS OF THE NUCLEATIONS AND THE IONIZATION OF THE ATMOSPHERE OF PROVIDENCE.

BY LULU B. JOSLIN.

1. *Introduction.* — The results obtained by Professor Barus,[1] showing a characteristic succession of the values of atmospheric nucleation throughout the year, suggested a parallel inquiry into the variations of the number of ions in the atmosphere in the lapse of time. The present work which will appear in full in the Carnegie Publications, was therefore undertaken at his instigation, and observations systematically carried forward from August, 1905, to April, 1906.

In addition to the main purpose in view, it was hoped that a number of subsidiary questions might be answerable. Thus a large part of the nucleation of Providence is of local origin and enters the atmosphere with other products of combustion. Initially these nuclei were either highly ionized themselves, or the atmosphere originally received an accession of ions and nuclei in proportional quantities. It is therefore of interest to inquire whether any of the ionization survives, or whether there is any connection observable between corresponding changes of the nucleation and the ionization of a given place. The results which are carefully tabulated in the present paper seem to show that there is no such connection whatever; or that the ionization is maintained by causes which are quite distinct from those which bring forth the nucleation. No evidence suggests that the ionization is either emitted or absorbed by the nucleation, whence it follows that the ionization arises from agencies wholly nonlocal or artificial.

Apart from these main purposes, the data are interesting as a continuous record of ionization (which will be supplemented in the future), though as yet, sufficient time has not elapsed to ascertain whether the opposition in the monthly positive and negative ionizations found in the sequel is real or incidental. Cf. Fig. 5.

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[1] Smithson. Contrib., XXXIV., No. 1651, 1906, Chap. IX. Carnegie Publications, No. 40, January, 1906, Chap. IV. and V.

Finally I may add that work to investigate a possible relation between the nucleation and the ionization of the atmosphere, was undertaken in Helgoland and on the coast of the Ostsee by Prof. G. Lüdeling[1] in 1902 and 1903, using Aitken's dust-counter.

The time during which observations were recorded (August 21 to September 16, 1902, June 17 to July 4, 1903) were insufficient to warrant general conclusions, however, apart from the interesting special investigations which Professor Lüdeling's paper contains. Reference should also be made to P. Langevin's[2] important discovery of slow-moving ions in the atmosphere; but comparisons of this nature are beyond my present purpose.

2. *Measurement of Nucleation.* — The number of nuclei in the atmosphere was measured by aid of the coronas of cloudy condensation, in the way fully described by Professor Barus (Smith's Contrib., l. c., Chap. 8) and the same apparatus which had proved efficient in the earlier investigations was used throughout the present experiments. Two or more observations were usually made daily, together with the meteorological elements of wind, weather and similar data. The ionizations referred below, § 7, were taken in the same place.

3. *Data for Nucleations.* — The tabulated data (which will here be omitted) show the day and month, the time in hours and tenths of an hour, the current weather, the direction of the wind and the temperature of the atmosphere in degrees Fahrenheit, etc. Further data referring to the coronas give the temperature of the fog chamber in degrees C., the diameters, $s$, of the coronas at the end of a radius of 30 cm. Hence $s/30$ is nearly their angular diameter when the eye and the source of light are at distances 85 cm. and 250 cm. on opposite sides of the fog chamber. Final data indicate the colors of the successive annuli of the coronas, reckoned from within outward, and the number of nuclei in thousands per cubic centimeter

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[1] Two papers in the Veröffentl. des Königlich Preussischen Meteorologischen Instituts, Berlin, 1904.

[2] P. Langevin, Bull. Soc. Franc. de Phys., May, 1905, p. 79.

deduced from the amount of water precipitated per cubic centimeter and the sizes of particles in successive coronas as listed by Professor Barus (l. c.).

### TABLE I.

*Average values, for successive months, of the number of nuclei, n, per cubic centimeter in the atmosphere of Providence, R. I.*

| Year. | Month. | $n \times 10^{-3}$ | Year. | Month. | $n \times 10^{-3}$ |
|---|---|---|---|---|---|
| 1905 | August. | 22.9 | 1905 | December. | 50.3 |
| | September. | 24.2 | 1906 | January. | 53.3 |
| | October. | 35.3 | | February. | 53.1 |
| | November. | 45.3 | | March. | 52.6 |

4. *Remarks on the Table of Nucleation.* — With regard to the individual observations very little can be adduced that has not already appeared in the earlier work. Conformably with the mild winter, the nucleation as a whole is relatively low, an unfortunate occurrence in its bearing on the purposes of the present work; but deductions of this character will be brought forward with advantage in connection with the daily and monthly mean nucleations below. It is rather curious that the forest fires on Cape Cod in the early May and the powder combustion on July 4 produces so little impression; on the other hand, the cold weather in August is at once marked by large coronas.

5. *Mean Daily Nucleation.* — The data of § 3 were then averaged for the successive days in the second table. The results are recorded graphically at the bottom of the charts, Figs. 1 to 4, where the current days appear as abscissas, the corresponding mean nucleations in thousand per cubic centimeter as ordinates. One may note the rare occurrence of the large *g-b-p* coronas so frequently met in the high nucleations of the preceding winter.

6. *Mean Monthly Nucleations.* — The data of the last table suffice for the determination of the average nucleations per month, care being taken to omit the days on which no observations were taken. Table I. contains the results.

These data are shown in the lower graphs of Fig. 5. What is remarkable is the gradual rise of the curve to a persistent maximum reaching nearly into April. True the winter was relatively mild and the spring relatively cold; but one would not be prepared to predict nucleations so uniformly maintained between November and April. The distribution is in fact peculiar, as may be seen by comparing it with the nucleation of the preceding years,[1] since 1902.

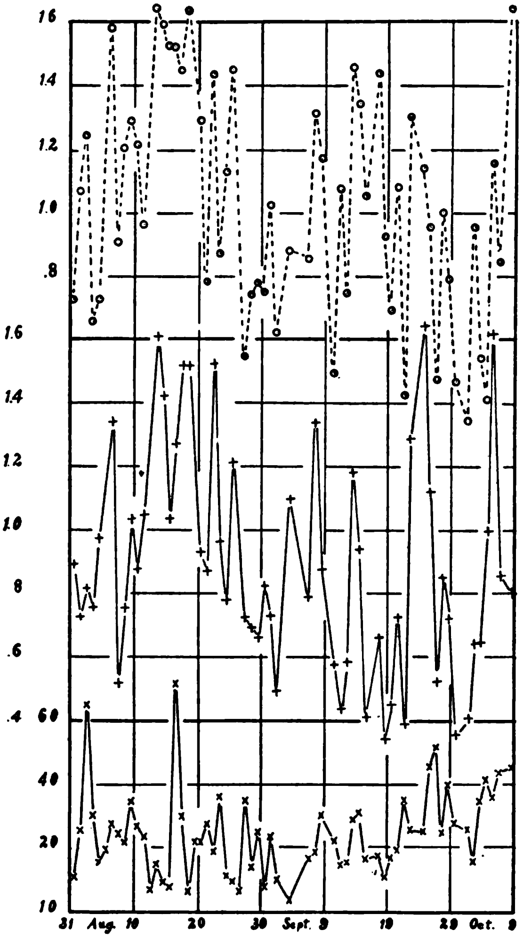

Fig. 1.

7. *Measurement of Ionization.* — To determine the number of ions in the atmosphere, Ebert's[2] well known apparatus was used. This consists of a tubular condenser, the inner coat of which is

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[1] Barus, Phys. Review, XXII., 1906, pp. 91, 92.

[2] H. Ebert, Illustr. Aëronaut. Mittheilungen, Oktober, 1902, pages 1 to 10.

charged and in contact with a graduated electroscope. The air to be examined is passed through the condenser by an aspirator-fan propelled by clock-work. The air delivery of the machine is also carefully standardized.

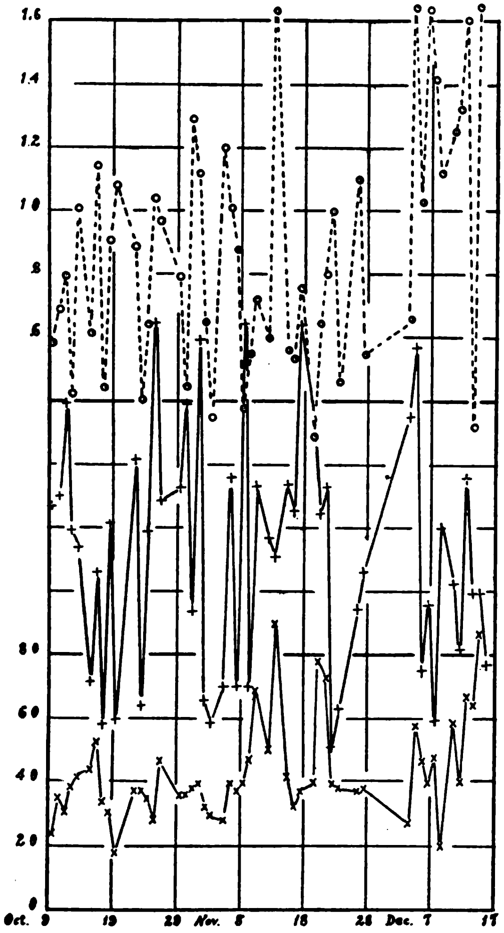

Fig. 2.

In order to test the same air which yielded the nuclei for the preceding measurement, the electrical apparatus was swung from the outside of a window on a long swivel bracket. In this way it could be drawn near the window for charging and examination with appropriate lenses, or moved to a reasonable distance away from the window during the passage of the air to be tested. In winter all measurements must clearly be made with a galvanoscope on the outside of the house.

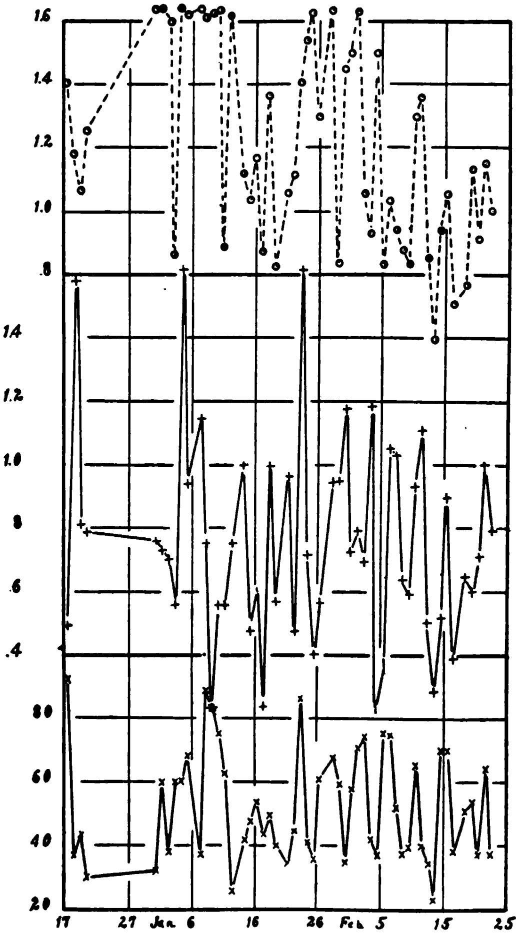

Fig. 3.

The difficulties encountered in using this apparatus in cold weather will be investigated later (§ 10). Here some reference to its constants is in place. The quantity of air passed through the condenser in the fiducial time (about 10 minutes) was $1.0357 \times 10^6$ cubic centimeters; the capacity of the condenser 17.74 cm. Hence if $V$ is the drop of potential in volts during the fiducial time specified

$$Q = 17.74 \frac{V/300}{1.0357 \times 10^6} = \frac{V}{17.52 \times 10^6}$$

denotes the charge in one cubic centimeter of air. As $3.4 \times 10^{-10}$ is the electrostatic charge per electron

$$n \times 10^{-3} = \frac{Q}{3.4 \times 10^{-7}} = \frac{V}{6}, \text{ nearly,}$$

shows the number of ions per cubic centimeter. Measurements to find their velocity were not made, as this would have carried me too far from the purposes of this paper.

I may add that a similar apparatus was installed, in which the winter indraft of cold air (through a condenser), measured by an anemometer, was utilized. The object here was to determine the hourly variations of ionization. Though many observations were taken their meaning is vitiated by the temperature discrepancy mentioned in § 10. For this reason, perhaps, a periodicity similar to the one discovered by Wood and Campbell[1] with stagnant air, was not detected. It need not, of course, be manifest with atmospheric air.

8. *Data for Ionization.* — The tabulated data contain the date and hour, the weather, etc., the fall of potential $V - v$ ($v$ being the fall in the absence if the aspirator air current) in volts during the ten minutes of observation. From this the charge $Q$ in electrostatic units per cubic meter, and the number of ions $n$, in thousands per cubic centimeter, were computed. The sign of the charges was indicated in each case, together with their ratio $(Q+/Q-)$. The correction $v$ is regarded as negligible.

9. *Remarks on the Tables.* — Perhaps the most expeditious way of digesting this large body of observations is to plot them graphically (as above) in relation to time. This was carefully done throughout, and the statements now to be made refer to this summary.[2] It is not probable that positive and negative ions will show the same fluctuations in number, but a general similarity in the trend of the curves may be anticipated.

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[1] Nature, April, 1906, p. 583.

[2] The daily means, Figs. 1–4, also elucidate the text.

Beginning with August, 1905, the positive and negative ionizations usually vary in the same sense though rarely in the same absolute magnitude. There being but two observations, as a rule, for the day, the nature of the fluctuations is not referable to periods; and indeed there is as liable to be a rise as a fall of values during the middle hours of the day. Towards the end of the month and in the beginning of September, there is an absence of agreement in the march of positive and negative ionizations. Frequently the variation of one ionization is apt to lag behind the other.

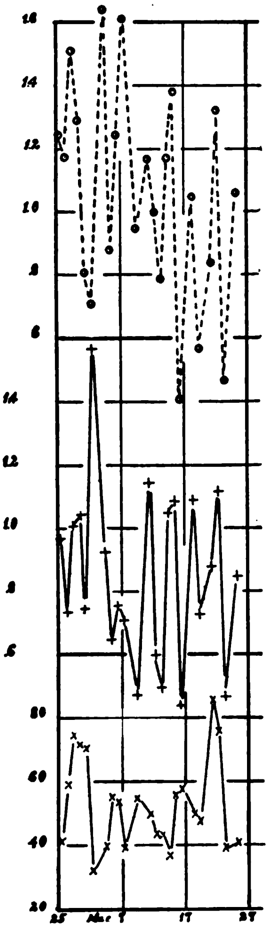

Fig. 4.

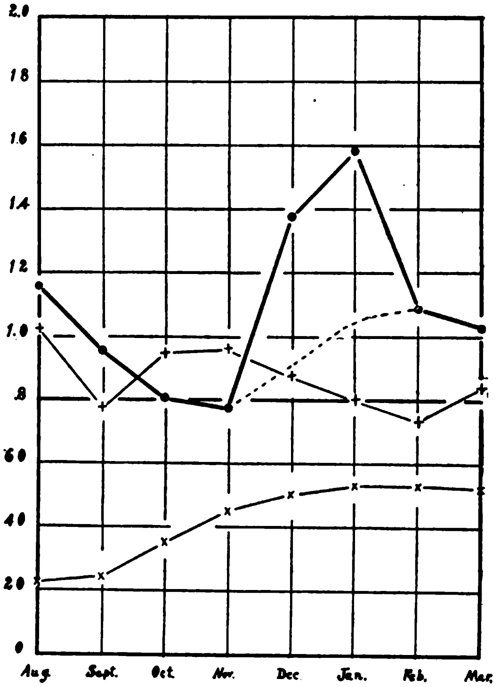

Fig. 5.

After the seventh of September the positive and negative variations tend to take the same sign again, but the agreement in the course of a month is less marked than before.

In October the earlier observations are as a rule in the same phase until October 10, where the first of a series of anomalies occur to be specially considered later (§ 10). While the data throughout the remaining part of October are regular, there are similarly displaced variations towards the end, which run quite into the next month.

During November similarity of variation of the positive and negative ionization may still be recognized, but in December the divergence of data is so marked that it is not possible to coördinate them; and the same discrepancy shows itself in January, both as regards the signs of variations and their absolute values. One may note moreover, that the positive curve, the observations for which were first taken, is more irregular in its march and fluctuates between relatively enormous values. Though there is some agreement in phase between January 18 and 25, the anomalies increase again at the close of the month.

The attempt was therefore made in February (§ 10) to account for and remove these discrepancies, and though this was but partially successful, the positive and negative results during the remainder of the season again return to an unmistakable agreement in character. There is moreover a curious parallelism between the general march of the nucleation curves and the ionization after February 15 as far as March. In the latter month the positive and negative ionizations, though at first fluctuating and uncertain, are finally in very close agreement.

From what has been stated it appears that the positive results during December and January are liable to be untrustworthy. The negative results, which were taken after the positive, show less irregular fluctuation and are in a measure acceptable throughout the eight months of observation.

10. *Errors of Measurement.* — The abnormal data during the occurrence of cold weather, and as a rule in December and January, show that some grave error must here have crept into the results. As every part of the condenser and appurtenances functioned fault-

lessly, this error is liable to be found in the galvanoscope. Changes of temperature produce vertical currents in the capsule which modify the deflections of the aluminum foils. In the mean ranges, one scale part of double deflection is equivalent to about six volts, or to one thousand ions per cubic centimeter. Hence the presence of any secondary disturbance like the one in question is of very serious consequence. Prior to measurement, the apparatus was naturally left in the cold air out of doors until temperature uniformity was presumable. But this is not sufficient as the special observations in the early part of February show, even for a galvanoscope dried with sodium.

Turning first to the leakages due to conduction, etc. ($v$ in the above equation), direct experiments made at different times showed values of .073, .067, .120 volts per minute, or less than .9 volts for the ten minutes of observation. This is equivalent to an excess of 150 ions per cubic centimeter. As it is applied equally to the positive and to the negative ions, is independent of the size of the deflections and the same, no matter whether the deflections on both sides are equal or not, it has no bearing on the outstanding errors in question. It was not deducted from the ionizations $n$ of Table I. which are therefore slightly too large.

Trials made between February 4 and 11 showed that in almost every case the first measurements (whether for positive or negative ions), even after the galvanoscope had been exposed to the cold air for some time, is too large. This discrepancy may at times extend to the second and third observations (February 6, 9, 11). Usually, however, the second and third observations are liable to be trustworthy (February 6, 10, 11, etc.). Hence electroscopic apparatus which cannot be left permanently out of doors, but is taken from a warm room into the cold atmosphere, even if it is sodium dried, is not liable to show warrantable results after mere waiting for uniform temperature. It seems additionally necessary to pass a large volume of cold air through the condenser, or to make successive measurements in series. The observer is usually in doubt, whenever the positive and negative ionizations differ widely, so that at least three tests must be made. The tendency of the apparatus to show spurious results is usually indicated by an inequality of deflections of the foils on either side of the vertical. They may increase to a maximum after charging and then decrease regularly. The latter probably finds an explanation in the gradual cessation of down-pouring cold air current near the sides of the capsule of the galvanoscope, but the persistence of unequal deflections must follow from other causes. Remembering that the air is desiccated internally with metallic sodium, it seems hardly credible that there can be a precipitation of moisture from this dried air on the aluminum foils; and yet the behavoir is such as if a moisture gradient from the foil nearest the sodium to that more remote, were permanently maintained. In such a case there would be slight but unequal precipitation of vapor on the two foils, in an apparatus passing from warm to cold, and persistence would be due to freezing. The only other explanation is the possibility of charges on the very cold glass and other insulators which cannot be earthed.

11. *Mean Daily Ionization.* — As in the preceding case, the observations were now averaged for single days. The results appear in special tables, here to be omitted as they are sufficiently given in the charts, Figs. 1 to 4, where the number of ions in thousands per cubic centimeter are laid off vertically, the upper graph referring to positive, the middle to negative charge. Very little that is new may be taken from these figures and their appearance in this place is to serve as a basis for the monthly ionizations which follow. In comparing the ionizations with the nucleation of the atmosphere, however, these charts serve a useful purpose. Thus it would be difficult to detect synchronism in the nucleations and ionizations of August, September, October, November, December. But from the middle of January to the end of February suspicions of this kind would be justified.

12. *Mean Monthly Ionizations and Conclusion.* — The straightforward way of arriving at a conclusion as to the presence or absence of a relation between the nucleation and the ionization of the atmosphere, consists in comparing the average monthly values for both cases. This is done in Table II., and graphically in Fig. 5.

The curve showing the distribution of negative ions is probably the more trustworthy, as these observations were made last. The positive distribution curve is too high in December and January for the reasons already stated, and its more probable course during these two months is indicated by the dotted line. It seems exceedingly curious, that whereas the fluctuations of positive and negative ionization in successive observations on the same or on succeeding days, usually show the same sign though not the same absolute value, this is not in general the case with the monthly ionizations. The two curves of Fig. 5 throughout the greater part of their course vary in opposite directions.

TABLE II.

*Average values, for successive months, of the number, n, of positive and of negative ions per cubic centimeter in the atmosphere of Providence, R. I.*

| Year. | Month. | $n \times 10^{-3}$ (positive ions). | $n \times 10^{-3}$ (negative ions). |
|---|---|---|---|
| 1895 | August. | 1.16 | 1.02 |
| | September. | .95 | .78 |
| | October. | .80 | .95 |
| | November. | .78 | .96 |
| | December.[1] | 1.38 | .88 |
| 1896 | January.[1] | 1.58 | .80 |
| | February. | 1.09 | .74 |
| | March. | 1.03 | .84 |

Compared with the uniform curve for nucleation, the appearance of the ionization curve is sufficiently distinctive. The only conclusion to be drawn from the results for the distribution of either the positive or the negative ions is this, that there is no discernible relation between the number of ions and the number of nuclei present in the atmosphere at any time, or that the two distributions result from entirely distinct causes. The ionization of a given region in the long run is independent of artificial local contributions, however abundant these may be.[2]

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[1] See § 10.

[2] As the negative ions are more easily "absorbed" by the nuclei than the positive ions, one might refer the descent of the graph from November to February to some such cause; but the curve as a whole does not bear this out consistently.

# THE CADMIUM STANDARD CELL.

By George A. Hulett.

A STANDARD cell with a low temperature coefficient was devised by Mr. Edward Weston in 1891.[1] By substituting cadmium sulphate and cadmium amalgam for the zinc sulphate and zinc of the Clark cell, it was found that the temperature coefficient of the cell was reduced 95 per cent., and when the solid cadmium sulphate was dispensed with and only a solution of cadmium sulphate used in the cell, the temperature coefficient was still less. With a solution saturated at 0° C., Barnes and Lucas found[2] that the E.M.F. of the cell was constant for all ordinary temperature changes. This latter combination is a valuable laboratory instrument, but is not sufficiently reproducible or constant to serve as a standard of E.M.F.

The Clark cell has a variation of E.M.F. of over a millivolt per degree, and for accurate work requires a very exact control of the temperature for a considerable time. The saturated cadmium cell has only one twentieth of the temperature coefficient of the Clark cell and many other desirable features, so that considerable work has been done in testing its reproducibility and constancy.

A. Dearlove[3] found that attention must be given to the cadmium amalgam and concluded that it was best to use a 12.5 per cent. amalgam, made by melting together one part of cadmium and seven parts of mercury. Since then considerable work has been done on cadmium amalgams. Kerp and Boettger[4] concluded that the solid which separates from cadmium amalgams of over 5 per cent. was a compound represented by the formula $Cd_2Hg_7$. However, from the work of Bijl[5] and Puschin[6] it appears that between about 5 and 15 per cent. of cadmium, the amalgam is a two-phase system, composed of a solid and a liquid phase, and that the solid phase is not a compound, but an isomorphous mixture of cadmium and mercury. The composition of this mixed crystal varies with the temperature, but has a definite composition and E.M.F. for each temperature. The result is that on adding cadmium to mercury, the E.M.F. of the amalgam, towards a cadmium sulphate solution, increases with the increasing per cent. of cadmium until the mixed crystal appears. If the temperature is constant, further additions of cadmium will not effect the E.M.F., but only the relative amounts of the two phases. When the liquid phase disappears a further addition of cadmium will increase the E.M.F. of the system. From Bijl's results this two-phase range is between 10 and 18 per cent. of cadmium at 50°, 5.3 to 15 per cent. at 25° and 4 to 14 per cent. of cadmium at 18°. Jaeger[1] showed that all amalgams in a two-phase range have, for a given temperature, the same E.M.F. almost to the limit of measurement, and it is this property that makes the cadmium amalgam valuable for a standard cell, since little attention need be given to the exact composition of the amalgam, only that it must always remain in the two-phase range for all temperatures at which the cell is used. The 12½ per cent. amalgam first proposed by Dearlove, l. c., satisfies these conditions and also has the desired solidity.

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[1] U. S. Patent No. 494,824. Applied for April 24, 1891.

[2] Jour. Phys. Chem., 8, 196, 1904.

[3] Electrician, 31, 645, 1893.

[4] Zeit. f. Amorg. Chem., 25, 1, 1900.

[5] Zeit. Phys. Chem., 41, 641, 1900.

[6] Zeit. f. Anorg. Chem., 36, 201, 1903.

It will be concluded from the above that there must be a temperature coefficient for the E.M.F. of the junction : Cd-amal. || cadmium sulphate solution. To test this the following combination was set up :

$$\begin{array}{c\|c\|c} \text{Cd amal.} & \text{CdSO}_4 \text{ solution sat. at } 4^\circ & \text{Cd-amal.} \\ 0^\circ \text{ C.} & \longrightarrow \qquad\qquad \longrightarrow & 30^\circ \text{ C.} \end{array}$$

This showed a thermoelectomotive force of .00917 V. in the direction of the arrow, also the following combination :

$$\begin{array}{c\|c\|c} \text{mercury} & =\text{Hg}_2\text{SO}_4 \text{ cadmium sulphate solution sat. at } 4^\circ \text{ C. Hg}_2\text{SO}_4 & \text{mercury} \\ 0^\circ \text{ C.} & \longrightarrow \qquad\qquad\qquad\qquad \longrightarrow & 30^\circ \text{ C.} \end{array}$$

showed the same .00917 V. and in both cases the cold metal was the anode. Therefore both legs of the cadium cell have a decided temperature coefficient, but when the directions of the electromotive forces at the two electrodes are considered, it will be seen that the two temperature effects are oppositely directed as far as the total E.M.F. of the cell is concerned, and it is merely a coincidence that the E.M.F. of the cadmium cell is so little affected by temperature changes.

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[1] Wied. Ann., 65, 106, 1898.

The amalgam may be made by depositing cadmium electrolytically in a weighed amount of mercury. An excess of cadmium is deposited, the amalgam weighed, and then the correct amount of mercury added to make it 12.5 per cent. Very pure cadmium is obtained in this way if recrystallized cadmium sulphate is used for the electrolyte. This method was devised and used for the amalgams of the (*D*) and (*F*) cells of 1903 but it has since been found that a trace of other metals, even zinc, has hardly a measurable effect on the E.M.F. of the cadmium amalgam and that ordinary pure cadmium answers every purpose. The later amalgams have been made by melting together one part of Merck's cadmium with 7 parts of pure mercury, and this was done on a water-bath with the metals covered with a cadmium sulphate solution.

Cadmium sulphate ($CdO_48/3H_2O$) is a well-defined salt and is easily obtained in large monoclinic crystals which do not seem to carry other salts isomorphously mixed.[1] The rate of growth of the crystals is very slow and the clear ones are quite free from inclusions, but in every crop there are many white crystals which grow more rapidly and may have inclusions. It is an easy matter to pick out the clear crystals and, due to their slow rate of solution, they may be thoroughly rinsed with water. In the work so far the cadmium sulphate crystals have been dissolved by grinding them in a mortar with water until a saturated solution was obtained. This solution was treated with a little cadmium carbonate to neutralize any excess of acid which might have been present. The solution was then carefully filtered and placed in a crystallizing dish to a depth of one centimeter, the dish was covered with thin filter-paper to keep out dust and the solution allowed to evaporate until a good crop of crystals formed. Samples of cadmium sulphate from various sources and with known impurities have been used, but it has been found that, after one crystallization and thorough rinsing that there was not a detectable difference in their behavior of the clear crystals in cadmium cells. The solution from these crystals is slightly acid as the result of hydrolysis, but the solution of these crystals in distilled water is exceedingly well-defined and reproducible and it has been found unnecessary and undesirable to change it in any way. Kohnstamm and Cohen[1] thought that they had detected a transition point for this salt at 15° C. but the changes on which they based their conclusion have been traced to the 1 to 6 amalgam used.[2] This strength amalgam is not a two-phase system below 23° and may undergo slow changes.

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[1] Retgers, Zeit. f. Phys. Chem., 16, 594, 1895.

The mercury used in all this work on standard cells has been distilled under diminished pressure with a current of air passing through with the mercury vapor. This method insures the removal of all oxidizable metals.[3]

## The Depolarizer.

The most extensive observations on the cadmium cell have been published by Jaeger and Lindeck.[4] From their results it seemed that the cadmium cell was reproducible to 1 or 2 parts in 10,000 and the authors attributed the observed variations to the fact that the mercurous sulphate used as polarizer was from different sources, just as Lord Rayleigh had previously[5] traced variations in the Clark cell to differences in the mercurous sulphate.

Commercial mercurous sulphate is usually made from solutions of mercurous nitrate and sodium sulphate. The precipitate is exceedingly finely divided and carries with it traces of the reagents and is acid. Also an insoluble basic salt is formed and, while these impurities are not present in large quantities, they increase the mercury in the solution made from such preparations and give too large a value to the E.M.F. of the cell.

A fine-grained powder is more soluble than a coarser-grained sample of the same salt, and while the fine-grained powder slowly becomes coarser-grained when left in contact with its solution, there is here a possible source of variation, as has been pointed out by

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[1] Wied. Ann., 65, 344, 1898.

[2] Cohen, Zeit. Phys. Chem., 34, 631, 1900, and Jaeger and Lindeck, Zeit. Instk., 21, 33, 1900.

[3] Phys. Rev., 21, 387, 1905.

[4] Zeit. f. Instk., 21, 33, 1901.

[5] Philos. Trans., 176, 781, 1886.

H. v. Steinwehr.[1] The "Board of Trade" specifications advise the washing of the mercurous sulphate with water, and while this removes some of the impurities, it also hydrolyzes some of the salt. A rather insoluble basic sulphate is left with the salt, while a soluble acid salt goes into solution, and the wash water with the acid salt is not entirely removed even by suction. It will be seen that the materials and methods which have been used in making the paste for cells afford abundant opportunity for variations. Experiments have shown that acids and particularly the basic salt cause irregular variations in the E.M.F. of the standard cells.

In 1903 the electrolytic method of preparing mercurous sulphate was devised by the author[2] and independently by Dr. F. A. Wolff, of the Bureau of Standards.[3] By this method pure mercurous sulphate, mixed only with dilute sulphuric acid and mercury, was obtained. The acid was removed either by washing with the saturated solution of cadmium sulphate or by using alcohol and ether. Both methods were effective in removing the acid and seemed to prevent hydrolysis. The first cells made with this properly washed electrolytic mercurous sulphate were four (*D*) cells on December 21, 1903, and 10 (*F*) cells on February 15, 1904. These cells agreed among themselves to 1 part in 100,000, assumed their constant value at once but were .00028 V. lower than cells made in the old way with commercial mercurous sulphate.

These cells seemed so much superior to those made according to the old specifications that attention was at once turned to thoroughly testing samples of mercurous sulphate made by the electrolytic method. In brief it was found that it was possible to use a very considerable range of acid strength and current density in making the sulphate. Also that the preparation was sufficiently coarse-grained to entirely avoid any effect due to the size of particles on the solubility, and that it was the most reproducible and reliable preparation for use in standard cells. The details of this work as well as a complete description of the method of preparing electrolytic mercurous sulphate and making the paste for cells have already been described.[1]

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[1] Zeit. f. Instk., 25, 201, 1905.

[2] Trans. Amer. Electrochem. Soc., 5, 59, 1904; Trans. Internat. Elect. Congress St. Louis, Vol. 2, 109, 1904; Zeit. Phys. Chem., 49, 483, 1904.

[3] Trans. Amer. Electrochem. Soc., 5, 49, 1904.

## SLOW CHANGES IN THE E.M.F. OF THE CADMIUM CELL.

After the (*D*) and (*F*) cells have been under observation for nearly two years, six cadmium cells, *A*1 to *A*6, were made and the materials and construction were, as nearly as it was possible to make them, a duplication of the (*D*) and (*F*) cells, ***but these new cells were .00011 V higher than the older ones.*** More cells were made with different samples of electrolytic mercurous sulphate and with variations in the other materials and in the construction, but they all agreed with the new (*A*) cells. Fortunately 10 Clark cells had been made in 1904, and with some of the same electrolytic mercurous sulphate which had served for the depolarizer of the (*F*) cells. These Clarks did not show the usual "ageing" but appeared to have their constant value at once. After two years, however, they appeared to have slightly increased in value (.00011 V.). The cadmium cells had been assumed constant and had been made the basis of all the comparisons. If now the Clarks had been assumed to be constant and taken as the basis, the cadmium cells would, of course, appear to have decreased by this .00011 V. and the difference between the new and the old cadmium cells is then explained by a slow change in the cadmium cell.

More Clark cells (*H*11 to *H*16) were made on July 30, 1905, and on February 25, 1906, cells *H*17 to *H*21 were made, and for depolarizer some of the same sample of electrolytic mercurous sulphate was used as had served for the new (*A*) cells. The following table gives some of the many observations that have been made on these cells. All the cells have been maintained in a large oil-bath since October, 1905. The bath was electrically heated and controlled and the temperature has remained constantly at 25° C. to within $\frac{1}{50}$°. For details see this journal, 22, 323, 1906. The basis of all the results given in this paper are the Clark cells, *H*1 to *H*21, which were made on three different dates and are now in good agreement. The value chosen is the one obtained by Dr.

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[1] PHYS. REV., 22, 321, 1906.

Guthe for these cells and is 1.42040 V. at 25° C.[1] This gives a calculated value of 1.43300 at 15° but it should be added that these Clark cells were all made with electrolytic mercurous sulphate as depolarizer; the paste was prepared as previously described,[2] and they are .00030 V. lower than Clark cells made in the old way with commercial mercurous sulphate.

| Cell. | Date. | Mar. 18,'04. | Mar. 24,'05. | Aug. 5, '05. | Dec. 14,'05. | Mar. 4, '06. | June 4,'06 |
|---|---|---|---|---|---|---|---|
| *D*4 | Dec. 21,'03. | 1.01842 | 1.01831 | 1.01928 | 1.01832 | 1.01832 | 1.01830 |
| *F*1 | Feb. 15,'04. | 42 | 31 | 27 | 30 | 32 | 29 |
| *F*2 | " | 42 | 32 | 26 | 31 | 30 | 15 |
| *F*3 | " | 42 | 32 | 28 | 32 | 31 | 34 |
| *F*4 | " | 42 | 31 | 28 | 32 | 32 | 27 |
| *F*5 | " | 42 | 32 | 32 | 31 | 33 | 33 |
| *F*6 | " | 42 | 32 | 27 | 32 | 33 | 32 |
| *F*7 | " | 42 | 32 | 28 | 34 | 32 | 32 |
| *A*1 | Oct. 21, '05. | | | | 1.01843 | 1.01843 | 1.01842 |
| *A*2 | " | | | | 43 | 43 | 42 |
| *A*3 | " | | | | 42 | 43 | 42½ |
| *A*4 | " | | | | 43 | 43 | 42½ |
| *A*5 | " | | | | 43 | 43 | 42½ |
| *A*6 | " | | | | 43 | 43 | 43 |
| *H*2 | Mar. 15,'04. | 1.42040 | 1.42040 | 1.42038 | 1.42038 | 1.42040 | 1.42039 |
| *H*3 | " | 40 | 37 | 38 | — | 40 | 39 |
| *H*4 | " | 40 | 38 | 37 | 40 | 43 | 42 |
| *H*6 | " | 39 | — | 42 | 37 | 40 | 42 |
| *H*7 | " | 41 | 41 | 44 | 38 | 40 | 40 |
| *H*8 | " | 41 | 40 | 41 | — | 40 | 40½ |
| *H*11 | July 30,' 05. | | | | 1.42040 | 1.42041 | 1.42039 |
| *H*15 | " | | | | 41 | 41 | 41 |
| *H*16 | " | | | | 41 | 41 | 42 |
| *H*17 | Feb. 25,'06. | | | | | 1.42039 | 1.42041½ |
| *H*18 | " | | | | | 39 | 42 |
| *H*19 | " | | | | | 40 | 42 |
| *H*20 | " | | | | | 38 | 37 |
| *H*21 | " | | | | | 43 | 41 |
| *C*1 | Nov. 21,'03. | 1.01868 | 1.01864 | 1.01858 | 1.01862 | 1.01861 | 1.01860 |
| *A*7 | Nov. 15,'06. | | | | 72 | 70 | 67 |

The results given in Table I. from December 14, 1905 on, are the observed values, but the values for March 18, 1904, March 24,

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[1] Phys. Rev., 21, 117, 1906.

[2] Phys. Rev., 22, 334, 1906.

1905, and August 5, 1905, have been recalculated, for the sake of comparison, from the observations which were made at 21° and 18°. These cells all follow the accepted temperature coefficient so closely that the calculated values are reliable, but the conclusive facts are based upon the observations made since October, 1905, when the control of the temperature and the conditions of comparison have been particularly exact.

It is to be observed that the new cadmium cells, *A*1 to *A*6, are now .00011 V. higher than the older (*F*) series, and that the values of the (*A*) cells are now very close to the values the (*F*) cells originally had. On the other hand the Clark cells, made on three different dates, are now all in excellant agreement. The depolarizers of the (*F*) cells and the *H*1 to *H*10 Clarks were all from the same sample, while the sample of mercurous sulphate which was used for the new *A*1 to *A*6 cells was also used for the Clarks *H*17 to *H*21. This indicates that the change observed in the (*D*) and (*F*) cells is not a peculiarity of the electrolytic mercurous sulphate. Further proof that the electrolytic mercurous sulphate is not at fault is at hand in the observations on some cadmium cells which were made in 1903 with commercial mercurous sulphate according to the old specifications. These cells have also changed as indicated by the record of cell *C*1 given in Table I. On November 15, 1905, cell *A*7 was made with commercial mercurous sulphate and according to the old specifications and it will be seen that this cell is now higher than the older (*C*) cell. All of the cells made with commercial mercurous sulphate and according to the old specifications were very high at first and showed the usual "ageing" for a month before becoming "constant."

In the literature there is some evidence of this "drift" of the cadmium cell, Mr. F. E. Smith[1] describes some cadmium cells which were made in April, 1902, and two years later another cell was made with exactly the same materials, but the new cell was .00007 V. higher than the older ones.

This observed change in the E.M.F. of the cadmium cell is small and slow and from a practical standpoint is of little consequence, but it is not to be overlooked when it comes to a question of a standard of electromotive force. The change seems to be more rapid at higher temperatures and especially does the depth of the paste in the leg of the cell play an important rôle. Some cells were made on November 29, 1904, with the paste only 3 or 4 mm. deep, the object was to make a cell with a smaller internal resistance. These cells showed the normal value of 1.01844 V. when first made, but began at once to noticably decrease. On January 10, 1905, they were 1.01839, April 4, 1905, 1.01811 and by June, 1905, were about 1.0177 V. and were very irregular, only two of these cells were retained and in December, 1905, they were 1.0172 and 1.01815, and now June, 1906, they are 1.0160 and 1.01813 respectively. It is to be noted that the (*F*) cells are no longer in as good agreement as when first constructed. The paste in the (*F*) cells is about 10 mm. deep and it is 20 mm. deep in the *A* cells and in all cells made since these facts appeared. It might be added that the (*A*) cells have not yet shown a decided change but it is probably only a question of time.

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[1] Electrician, 53, 832, 1904.

From the foregoing it is to be concluded that slow changes take place in the cadmium cell and, during the past two years, a number of results have been obtained which indicate that it is the system in the cathode leg of the cell which is not in equilibrium. Mercurous sulphate has been formed electrolytically in a cadmium sulphate solution. The apparatus and method was the same as used for preparing electrolytic mercurous sulphate.[1]. The mercury from the anode went into the cadmium sulphate solution and separated as mercurous sulphate while cadmium was deposited at the cathode, the solution remained neutral and was saturated as cadmium sulphate crystals were present. The idea was that this preparation might be used directly in the cell without removing the mother liquor. It was expected that with this method and the rapid stirring that the product obtained would be in equilibrium with the cadmium sulphate solution and the mercury. Two samples were prepared and different current densities were used. The preparations were white and sufficiently coarse-grained to avoid the effect of size of particles on the solubility. One sample was made with a current density of .12 amp. per 100 cm.$^2$ mercury anode surface, and was used, with some of the solution in which it was made, for the depolarizer of cell *A*17. Some of this same sample was used for cell (*A*18) but its solution was first removed by suction and then it was washed with a fresh cadmium sulphate solution. The second sample was made with a current density of .5 amp. and was used direct in cell *A*19. These cells were made November 23, 1905, and the following results have been obtained:

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[1] PHYS. REV., 22, 334, 1906.

| Cell. | Nov. 30. | Dec. 14. | Jan. 1, 1906. | Feb. 7. | Mar. 4. | Apr. 13. | May 12. | June 4. |
|---|---|---|---|---|---|---|---|---|
| *A*17 | 1.10878 | 1.01872 | 1.01871 | 1.01870 | 1.01873 | 1.01871 | 1.01869 | 1.01868 |
| *A*18 | 86 | 78 | 75 | 67 | 65 | 60 | 58 | 55 |
| *A*19 | 48 | 48 | 47 | 49 | 48 | 49 | 48 | 48 |

It will be seen that the samples made with the different current densities do not agree and that the one made with the larger current density (*A*19) has remained quite constant and is nearest to the *A*1 to *A*6 cells. The sample which was made with a low-current density was used in cell *A*18, but the solution in which it was made was first removed by suction and then the salt was washed with a fresh cadmium sulphate solution. This cell was high at first and has decreased the most.

Two years ago an attempt was made to bring mercurous sulphate into equilibrium with a cadmium sulphate solution and mercury. The system — cadmium sulphate, mercurous sulphate, mercury and saturated solution — was rotated at 25° for ten days, and then the mercurous sulphate was brought onto a filter and washed with a fresh solution of cadmium sulphate. With this preparation three cells were made on May 6, 1904, and the following observations, calculated to the present basis and 25°, have been made:

| Cell. | May 6. | May 9. | June 13. | July 13. | Aug. 9. | Apr. 14, 1904. | June 3. | July 25. |
|---|---|---|---|---|---|---|---|---|
| *I*6 | 1.01975 | 1.01934 | 1.01900 | 1.01889 | 1.01887 | 1.01817 | 1.01800 | 1.01816 |
| *I*7 | 77 | 32 | 01 | 88 | 91 | 15 | 1797 | 1799 |
| *I*8 | 63 | 31 | 03 | 93 | 96 | 32 | 1807 | 1818 |

The cells had become irregular and had not become constant and it was concluded that the system, which had been rotated ten days, had not reached equilibrium, so the observations on these cells were discontinued. This question was taken up again after the "drift" in the (*D*) and (*F*) cells has been detected. It was decided to rotate this system in the cathode leg until it should come to equilibrium. When this point is reached there should be no further change in the solution or in the E.M.F. between the system and mercury. It was found most convenient to measure the E.M.F. at frequent intervals as a means of deciding on the absence of further change in the system.

An adjustable cadmium cell was made as represented by Fig. 1, the leg (*A*) contained the cadmium amalgam and the cadmium sulphate of the anode, and it will be seen from the cut that the side tube (*B*) of this leg bends down and passes through the neck of the tube (*C*). This tube (*C*) contained the mercury, paste and cadmium sulphate of the cathode leg of the cell. This cell was used in a water-bath and it was found necessary to attend to the insulation.

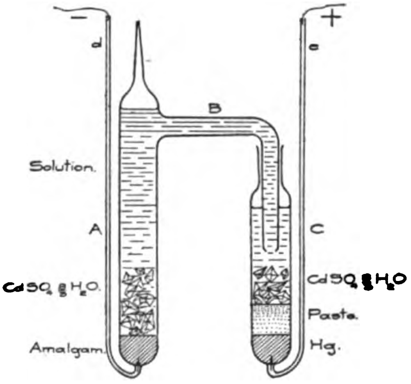

Fig. 1. (⅓ nat. size.)

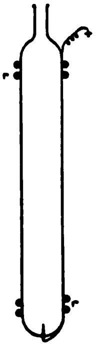

Fig. 2. (⅙ nat. size.)

This was done by sealing on the little tubes (*e*) and (*f*) as indicated in the cut, the contact wires passed up through these tubes and there was then no further trouble on this point. This cell had the value 1.01837 and has remained perfectly constant, although it has many times been taken apart and the anode leg used to test other systems. The cell is now six months old and a new anode leg has lately been made, but it shows exactly the same value as the older ones.

A large tube, 5 × 24 cm. (Fig. 2), contained the materials of the cathode system of the cadmium cell. The neck of this tube was made to admit the side tube (*B*) of the adjustable anode (*A*), Fig. 1, thus forming a cadmium cell. Contact with the mercury in this large tube was made through a platinum wire which was fused through the closed end of the tube and passed up on the outside. The wire was covered with shellac, a thin strip of cloth was placed over the wire and then it was thoroughly shellaced and finally covered with a coat of collodium (the use of collodium was suggested by Dr. E. H. Loomis and is a very admirable device for protecting anything which is to be in contact with water for any length of time). This large tube contained 140 gr. of mercury, 50 grams of coarse-grained electrolytic mercurous sulphate which had been washed with alcohol and dried, 50 gr. of cadmium sulphate crystals and about 400 c.c. of a saturated solution of cadmium sulphate. In order to bring this system to equilibrium, the neck of the tube was securely closed with a cork and rubber covering, the tube was brought to a horizontal position in the 25° bath and rotated about its longer axis as follows: Above the bath was a shaft which was run at any desired speed by a worm gear, and from this shaft two little belts extend down into the bath. The tube was suspended in the loops of these belts. The belts were kept in place by rubber rings on the shaft and on the tube. In this way it was possible to rotate the tube about its longer axis at any desired speed, the solid contents of the tube were spread out in a long layer and slowly "rolled down hill" as the tube rotated. This method insured a thorough mixing of the contents of the system and was sufficiently gentle to avoid grinding the solids. A fine powder has an abnormal solubility and this error is very considerable when the solubility is small. Also it was found desirable to avoid breaking up the mercury into small globules, because these globules formed larger ones when the rotation was stopped, and this change caused very decided variations in the E.M.F. readings. It was found that by rotating the tube at the rate of one revolution in about six seconds that the mercury generally remained in one globule, and that this rate, with the above method, still insured a perfect mixing of the contents of the tube. From time to time the tube was brought to an upright position in the bath and the E.M.F. measured with the aid of the adjustable anode leg. The large 100 liter thermostat maintained the temperature constantly within .02° of 25° C. Since the rotating would unduly expose the mercurous sulphate to the light, it was decided to avoid this possible source of error by covering the tube with asphalt paint and then with collodium.

The first rotation was for twelve hours, when the system was tested with the anode leg the first reading

| | | | | |
|---|---|---|---|---|
| 3 | minutes | after stopping | the rotation was | 1.0190 V. |
| 9 | " | " | " | 1.0184 |
| 35 | " | " | " | 1.0178 |
| 3 | hours | " | " | 1.0177 |

The system was now rotated three days and

| | | | | | |
|---|---|---|---|---|---|
| 5 | minutes | after stopping | the rotation | the E.M.F. was | 1.01938 V. |
| 20 | " | " | " | " | 1.01942 |
| 1 | hour | " | " | " | 1.01941 |
| 5 | " | " | " | " | 1.01941 |

The tube was closed and rotated seven and one half days, making a total of eleven days.

| | | | | | |
|---|---|---|---|---|---|
| 3 | minutes | after stopping | the rotation | the E.M.F. was | 1.01820 V. |
| 9 | " | " | " | " | 1.01860 |
| 30 | " | " | " | " | 1.01910 |
| 3 | hours | " | " | " | 1.01971 |
| 24 | " | " | " | " | 1.01971 |

The preliminary low values observed here were regarded as due to the mercury being in small globules and as they united to form larger ones the E.M.F. increased to a maximum. That the constant value obtained was reliable is shown by the following test. Some of the clear solution was removed and brought into a tube like the tube (*C*) of Fig. 1. Some mercury was put in to serve as an electrode and then the solution tested with the anode leg. The value obtained was 1.01983.

The system was now rotated six and one half days, making a total of seventeen and one half days.

| | | | | | |
|---|---|---|---|---|---|
| 3 | minutes | after stopping | the rotation | the E.M.F. was | 1.01920 V. |
| 5 | " | " | " | " | 85 |
| 30 | " | " | " | " | 91 |
| 1 | hour | " | " | " | 89 |
| 5 | " | " | " | " | 90 |
| 24 | " | " | " | " | 79 |
| 72 | " | " | " | " | 74 |

The clear solution was tested as previously described and gave 1.01992 V. Evidently a change begins to take place in the layer next to the mercury as soon as the solids settle down on the electrode and this is possibly the "drift" of the cadmium cell at its maximum rate.

The tube was again closed and rotated for eight and one half days, making a total of 26 days. The following readings were then obtained:

| | | | | | |
|---|---|---|---|---|---|
| 3 | minutes | after stopping | the rotation | the E.M.F. was | 1.0120 V. |
| 6 | " | " | " | " | 1.0155 |
| 18 | " | " | " | " | 1.0166 |
| 1 | hour | " | " | " | 1.01910 |
| 3 | " | " | " | " | 1.01976 |
| 7 | " | " | " | " | 1.01977 |
| 24 | " | " | " | " | 1.01973 |
| 48 | " | " | " | " | 1.01967 |
| 170 | " | " | " | " | 1.01948 |

Here the preliminary low value, which has been attributed to changes in the mercury electrode, was more persistent and the maximum value observed was consequently lower. After the tube had stood quietly for a week, the lower end was given a rotary motion in order to break up the mercury into smaller globules but without mixing the entire contents of the tube.

| | | | | | |
|---|---|---|---|---|---|
| 2 | minutes | after the shaking | just mentioned | the E.M.F. was | 1.0135 V. |
| 7 | " | " | " | " | 1.0161 |
| 12 | " | " | " | " | 1.0177 |
| 45 | " | " | " | " | 1.0196 |
| 1 | hour | " | " | " | 1.01985 |
| 2 | " | " | " | " | 85 |
| 6 | " | " | " | " | 85 |

These results indicate that the preliminary low values observed in the preceding experiments were due to the mercury changing from small to large globules, as had been assumed. It was possible to still further test this point as follows. The tube was rotated as before for three and one half days at the rate of one revolution in six seconds and then the rate was decreased to one revolution in seventy seconds and this rate of rotation was continued for one day in order to allow the mercury to collect in one globule. The tube was then carefully brought to an upright position and the anode leg adjusted.

| | | | | | |
|---|---|---|---|---|---|
| 2 | minutes | after stopping | the rotation | the reading was | 1.01977 V. |
| 4 | " | " | " | " | 77 |
| 10 | " | " | " | " | 78 |
| 40 | " | " | " | " | 76 |
| 1½ | hours | " | " | " | 75 |
| 5 | " | " | " | " | 71 |
| 9 | " | " | " | " | 68 |
| 24 | " | " | " | " | 64 |
| 48 | " | " | " | " | |

The clear solution gave 1.01985. It is evident from the preceding experiments that if the system in the cathode leg of the cadmium cell is stirred until no further change takes place that, at 25°, the cell has the value 1.0198 V. or .0014 V. higher than the cadmium cell. If this system, after it has been rotated until no further change takes place, be allowed to rest, the E.M.F. begins to drop but the clear solution, from which the solids have settled, continues to retain its high E.M.F. against a mercury electrode. It seems reasonable to conclude that there is some interaction between the cadmium sulphate solution and the mercurous sulphate which produces an increase in the mercury concentration of the solution, but when the solids settle down on the mercury, another change takes place at the boundary between the mercury and the paste which causes a decrease in the mercury concentration of solution next to the mercury. The possibility, that the oxygen of the air dissolved in the solution produces some mercuric mercury, has been considered. This would explain the results obtained if we assume that the mean rate of oxidation is rapid compared to the subsequent rate of reduction by the mercury. However I have not been able to get experimental proof of this view, while the following results with the cathode system of the Clark cell show that under similar conditions, oxidation by dissolved air does not play a measurable rôle in the case of a zinc sulphate solution. It seems more probable that the interaction between the cadmium sulphate solution and mercurous sulphate is of the nature of an hydrolysis accompanied by the slow formation of a new, slightly soluble solid phase. The evidence for this view will be given when the present experiments are completed.

In order to test the method that has been employed in the preceding experiments and also to confirm many of the conclusions, it was decided to subject the cathode system of the Clark cell to the same processes. An adjustable Clark cell was made similar to the above adjustable cadmium cell. This Clark cell has shown a constant value of 1.42045 V. at 25°. A large rotating tube was charged with mercury, mercurous sulphate (electrolytic washed with alcohol and dried), recrystallized zinc sulphate, and the saturated solution. This system was rotated as previously described and after twelve hours the contents were tested with the adjustable anode of the Clark cell, with the following results:

3 minutes after stopping the rotation the E.M.F. was 1.42052 V.
45 " " " " 1.42048
3 hours " " " 1.42048
6 " " " " 1.42049

The system was now rotated twenty-four hours and then showed 1.42050 V. and after the solids had settled some of the clear liquid was tested against a mercury electrode with the adjustable anode and the value obtained was 1.42051 V.

The system was now rotated for six days.

3 minutes after stopping the rotation the E.M.F. was 1.42055 V.
6 hours " " " 1.42050
27 " " " " 1.42054

The tube was again closed and rotated for 10 days, making a total of seventeen and one half days, and then gave the value of 1.42052 V. and was constant. This experiment shows that the cathode system of the Clark cell comes to equilibrium in less than twelve hours and remains constant from then on. The slight variations observed may readily be accounted for as due to slight temperature variations to which the E.M.F. of the Clark cell is very sensative, besides no special precautions were taken to exclude the effect of light, so the test was a very severe one.

These results obtained by rotating the cathode systems of the cadmium and Clark cells seem to confirm in a most decisive manner the validity of the observations of the last two years on the Clark and cadmium cells. The assumption that the "drift" of the E.M.F.

of the cadmium cell is due to changes in the cathode system seems justified, but the possibility that some of the observed decrease in E.M.F. might be at the amalgam of the anode, has not been overlooked. This was tested as follows: some of the old cadmium cells which are now distinctly lower than when they were first observed, were opened and the side tube (*B*) of the anode leg (*A*) of Fig. 1 was brought into contact with the liquid of the cell and the E.M.F. of the cathode leg measured with the new anode as well as with the old. Any difference in the E.M.F. would be due to differences between the old and the new anode.

| Cell. | With the Old Anode. | With the New Anode. |
|---|---|---|
| *F*1 | 1.01832 | 1.01829 |
| *F*2 | 1.01830 | 1.01830 |
| *F*4 | 1.01833 | 1.01830 |
| *C*2 | 1.01832 | 1.01827 |
| *N*9 | 1.01616 | 1.01617 |

Cell *C*2 was made on November 21, 1903, with commercial mercurous sulphate, and was originally 1.01866. Cell *N*9 was one of the cells made in November, 1904, with only a little paste and is still decreasing. With the new anode the cells are about .00003 V. *lower*, so the change at the cathode has been even greater than indicated by the direct comparisons of the cells.

The foregoing experiments justify the conclusion that the cathode system of the cadmium cell, as at present constructed, is not a system in equilibrium and that the E.M.F. of the cell decreases with time. The rate of this "drift" depends on a number of factors, but if the paste in the cathode leg is about 2 cm. deep, the change is very slow. The cadmium cell, when properly constructed with electrolytic mercurous sulphate, which has been prepared and washed as previously described, has a value of 1.01843 V. at 25° C. and seems to be reproducible to about 2 parts in 100,000. Cells should be made from time to time to detect the presence and magnitude of the drift. For all ordinary purposes this cell is entirely satisfactory but, if there are no serious errors in the experiments recorded in this article, the cadmium cell as at present constructed can hardly supplant the Clark cell as a primary standard of E.M.F.

The Clark cell made with recrystallized zinc sulphate and electrolytic mercurous sulphate which has been prepared and washed as described in this journal[1] has the value 1.43300 V. at 15° C. as determined by Dr. K. E. Guthe.[2] This value is also the average of all the best previous determinations of the value of the Clark cell in absolute units. The experiments described in this article have severely tested the Clark cell and with most favorable results. Several improvements and simplifications of this cell have been suggested by the work done are now being tested.

PRINCETON UNIVERSITY,
June, 1906.

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[1] PHYS. REV., 22, 334, 1906.
[2] PHYS. REV., 22, 117, 1906.

# PROCEEDINGS

# OF THE

# AMERICAN PHYSICAL SOCIETY.

## MINUTES OF THE THIRTY-THIRD MEETING.

A JOINT meeting of the Physical Society with Section B of the American Association for the Advancement of Science was held in the Physical Laboratory of Cornell University, Ithaca, N. Y., June 29 to July 3, 1906.

Vice-president Sabine, of Section B, presided.

The following papers were presented:

1. A Young's Modulus Apparatus. B. B. BRACKETT.
2. Lecture Room Resistance Apparatus. B. B. BRACKETT.
3. Two Neglected Factors in the Determination of Musical Quality. WALLACE C. SABINE.
4. Silver Perchlorate as the Electrolyte for the Silver Coulometer. HENRY S. CARHART, H. H. WILLARD and W. D. HENDERSON.
5. A Lecture Experiment in Electrolytic Thermo-Electromotive Force. HENRY S. CARHART.
6. Note on the Graphical Representation of Non-Sinusoidal Alternating Currents. FREDERICK BEDELL.
7. The Dispersion of Silver Chloride. E. F. NICHOLS and W. S. DAY.
8. Properties of Electric Charges on Moving Conductors. E. F. NICHOLS.
9. The Separation of Electric Charges in a Metal by Centrifugal Acceleration. E. F. NICHOLS.
10. Comparative Observations on the Evolution of Gas from the Cathode with the Glow Current in Helium and Argon. CLARENCE A. SKINNER.
11. The Effect of Absorbed Hydrogen on the Photo-Electric Current. W. P. HOLMAN.
12. The Production of Ozone by the Becquerel Rays. HARRY S. HOWER.
13. The Production of Ozone by the Photo-Electric Current in Oxygen. HARRY S. HOWER.
14. Fluorescence Absorption in Resorufin. FRANCES WICKE.
15. Further Experiments on the Phosphorescence of Sidot Blende. E. L. NICHOLS and ERNEST MERRITT.

16. Magnetograph Records of Earthquakes with special reference to the San Francisco Earthquake of April 18, 1906. L. A. BAUER.

17. Rotation and Elliptic Polarization Produced by Iron Films in a Magnetic Field. W. D. HARRIS. Presented by CLARENCE A. SKINNER.

18. Coefficients of Linear Expansion at Low Temperatures. H. G. DORSEY.

19. New Diffraction Spirals. A. G. WEBSTER.

20. The Calibration of Capillary Tubes. WILLARD J. FISHER.

21. The Latent Heat of Recalescence in Iron and Steel. FRANK K. BAILEY.

22. Thermal and Electrical Effects in Soft Iron between 100° and 218° C. EDWIN H. HALL.

23. Note on Certain Aspects of Drude's Electronic Theory of Metallic Conduction. EDWIN H. HALL.

24. The Capacity and Resistance of Aluminum Anode Films. C. McC. GORDON.

25. Spark Potentials in Liquid Dielectrics. ROBERT F. EARHART.

26. Spark Potentials between a Point and a Plane for Small Distances. ROBERT E. EARHART.

27. Electric Double Refraction in $CS_2$ at High Temperatures. L. S. MORSE.

28. Electric Double Refraction in $CS_2$ at Low Potentials. L. S. MORSE.

29. A New Alternating Current Galvanometer. L. A. FREUDENBERGER.

30. The Temperature of the Moon. WM. W. COBLENTZ.

31. Infra-Red Reflection Spectra. WM. W. COBLENTZ.

It was decided to hold the fall meeting of the Society in Chicago.

Adjourned. ERNEST MERRITT,
*Secretary.*

## TALBOT'S LAW AS APPLIED TO THE ROTATING SECTORED DISK.[1]

BY E. P. HYDE.

IT is evident that in photometric measurements some method other than varying the distance would be of value in comparing the illumination due to light sources of different intensities. The rotating sectored disk offers such a method, but at once brings up the question of the accuracy of Talbot's law.

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[1] Abstract of a paper presented at the Washington meeting of the Physical Society on April 20, 1906.

It was therefore decided to investigate this law in its photometric application, namely, to determine whether the photometric effect of the light transmitted through a rotating sectored disk is proportional to the total angular opening of the disk. Previous work has been done on this subject by Plateau, Helmholtz, Fick, and others, and more recently by Ferry and Lummer and Brodhun.

Ferry verified the law for white light, but found errors of considerable magnitude when the lights compared were different in color. A thorough study of his work led to the conclusion that a number of experimental errors had been introduced. A more satisfactory investigation was made by Lummer and Brodhun who found the law verified but did not carry their research as far as seemed desirable.

A choice of the Nernst glower as a light source, led to a preliminary theoretical investigation to determine errors in its use, due to the assumption of the inverse square law. In connection with this a study was made of the radiation from a cylindrical source.

In the experimental work, a photometric bench of the ordinary Reichsanstalt form was used, with a Lummer-Brodhun photometer head. The electrical measurements were made on a potentiometer.

The glower of direct current type was mounted without globe or ballast, so that it could be rotated in a horizontal plane, the latter containing the photometric axis. In the measurements the glower was turned first with one side toward the photometer, then through 180 degrees, the mean of the two sets of readings being taken. To avoid air currents it was covered with a tall cylindrical hood carefully blackened and fitted with black velvet to prevent reflection. Another glower similarly mounted was used for a comparison lamp, being rigidly connected to the photometer head by two adjustable rods.

The substitution method was used, readings being taken with the disk in and out, the distance from the test glower to the photometer head being altered in the proper proportion.

The disks employed were accurately measured and were mounted on and driven by a small electric motor. The range of total openings was from 288 degrees to 10 degrees. To study the effect of color, red, green and blue glasses were inserted in succession in the eye piece of the photometer. Readings were also made with the Nernst used as a comparison lamp replaced by an incandescent lamp at low voltage.

Elaborate precautions were taken to eliminate all possible sources of error such as those due to distance, inequality of the ways, reflections, intensity of illumination, speed of the disks, the personal equation, etc.

The results obtained were plotted in the form of a curve, having angular openings as abscissæ and percentage deviations from the law of Talbot as ordinates. It was shown that for all angular openings the law is verified for white light to within 0.3 per cent., which probably represents the limit of accuracy of the observations. It is verified also for colored light, and for difference in color between the sources, but not to such a high degree of accuracy.

## Note on the Compound Interferometer.[1]

By C. W. Chamberlain.

In an article on "Short Spark Discharges" in *Phil. Mag.* (6), Vol. 9, p. 696 (1905), Professor C. Kinsley presents the following equations showing the relation between the actual movement of the carriage and the increase in the length of the path of the ray.

Let $\alpha$ = angle of incidence.
$x$ = angle between mirrors $A$ and $B$.
$D_n$ = actual distance passed over by the ray between the mirrors due to a movement of the mirror $B$.
$n$ = the number of the order, *i. e.*, $n$, gives the number of times the ray is reflected by the mirror $B$.
$d$ = actual movement of the mirror $B$ along the original path of the ray.
$f_n$ = number of fringes that passed the cross hair of the microscope when the $n$th order of reflections was used.
$\lambda$ = wave-length of the light employed.
$a = d \cos \alpha$.

$$D_5 = \frac{4a}{\cos \alpha} + \frac{4a}{\cos (\alpha - 2x)} + \frac{2a}{\cos (\alpha - 4x)}.$$

$$D_{10} = 4a\left\{\frac{1}{\cos \alpha} + \frac{1}{\cos (\alpha - 2x)} + \frac{1}{\cos (\alpha - 4x)} + \frac{1}{\cos (\alpha - 6x)} + \frac{1}{\cos (\alpha - 8x)}\right\}.$$

$\alpha = 22\frac{1}{2}°$. For the tenth order $x = 2\frac{1}{2}°$.

Substituting in the above equations,

$$d = \frac{D_{10}}{19.09}.$$

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[1] Abstract of a paper presented at the Washington meeting of the Physical Society on April 21, 1906.

The above equations are based upon a misconception. The general equation is as follows:

$$D_n = 2d \cos nx \cos (n-1)x \left( \frac{1}{\cos nx \cos (n-1)x} + \frac{1}{\cos (n-1)x \cos (n-2)x} + \frac{1}{\cos (n-2)x \cos (n-3)x} + \cdots \frac{1}{\cos x} \right).$$

It thus appears that the sparking distances as measured by Professor Kinsley are 6.6 per cent. too small where he employed fringes of the tenth order, and 7.7 per cent. too small where he employed fringes of the fifth order.

## COMPARATIVE OBSERVATIONS ON THE EVOLUTION OF GAS FROM THE CATHODE IN HELIUM AND ARGON.[1]

BY CLARENCE A. SKINNER.

As aluminium and magnesium have been found to give off as cathodes hydrogen much more freely than the denser metals these were chosen for making the comparative observations in helium and argon.

Under an uninterrupted series of experiments six different cathodes of aluminium (circular disks, diam. 15 mm.) were tested — three in helium, and three in argon — with electric currents of one, two, and three milliamperes respectively in each gas. Observations were made on the change of gas pressure with duration of current. Notwithstanding the fact that the cathode fall in helium under the existing conditions was, for the same current, at least twice that in argon and hence the heating effect at the cathode twice as great, the rate of evolution of gas was practically the same in the two gases. With a current of one milliampere the evolution in the two gases was practically identical for the first nine minutes and also for the same period there was perfect agreement in rate with Faraday's law. At the end of fifteen minutes the results from argon were less than ten per cent. below the required value, while those from helium were somewhat lower still. With a current of two milliamperes, the evolution in helium was, during the first minute in excess, that in argon in agreement with the law. After that time and up to the end of six minutes the results in both followed the required rate, falling short gradually thereafter. With three milliamperes the results in both gases were excessive for the first minute, agreed with the law during the next two, then fell short rapidly thereafter. In each case about .05 c.c. of gas (atmospheric pressure) was given off from each square centimeter of aluminium before the rate of evolution fell below Faraday's law.

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[1] Abstract of a paper presented at the Ithaca meeting of the Physical Society, June 29–July 3, 1906. To be published in full in Phil. Mag.

Similar results were obtained with magnesium cathodes.

These experiments support the assumption made earlier that the rate of evolution of gas from a given cathode is the same in different gases, and therefore tend to establish the fact that certain gases are absorbed by the anode likewise at a rate determined by Faraday's law.

## PERCHLORATE OF SILVER AS THE ELECTROLYTE IN A SILVER COULOMETER.[1]

BY HENRY S. CARHART, H. H. WILLARD AND W. D. HENDERSON.

THE object of this research is to find an electrolyte if possible that will be free from the difficulties presented by silver nitrate. These are, the looseness of the deposited crystals, leading to loss in washing, and the formation of a heavy anodic liquid, which must be kept away from the cathode as completely as possible. The research is made more important just at present by the reaffirmation of the definition of the international ampere in terms of the deposit of silver by electrolysis.

One of us (Mr. Willard) has devised a method of preparing the perchlorate of silver ($AgClO_4$) in a pure state, and we have made a fairly large number of trials to determine its behavior in comparison with silver nitrate in electrolysis. The results are encouraging, but a large amount of patient work must be done before any decided conclusions can be reached.

The starting point in the preparation of perchlorates is sodium perchlorate, which is now obtainable commercially. It may be readily made in large quantities in the laboratory by the electrolysis of sodium chlorate.

A saturated solution of the perchlorate is diluted with two and a half times its volume of hydrochloric acid and is then saturated with the gas. Most of the sodium is precipitated as chloride. The solution of hydrochloric and perchloric acids is evaporated until heavy white fumes appear. The residue then contains about sixty per cent. perchloric acid and a little sodium perchlorate. This crude product is then distilled, preferably in a vacuum. It can be distilled under atmospheric pressure, but it then suffers a little decomposition, with the production of chlorine and its oxides. These dissolve in the distillate and they may be removed by aspirating air through the warm solution.

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[1] Abstract of a paper presented at the Ithaca meeting of the Physical Society, June 29–July 3, 1906.

To prepare silver perchlorate a suitable quantity of silver nitrate is weighed out and an amount of perchloric acid slightly in excess of the theoretical requirement is added. The temperature is gradually raised until the nitrate has dissolved and nitric acid is freely evolved. Finally the mass is maintained at 250° C. for several hours to remove the last traces of perchloric acid. A little chloride is formed at this temperature; but if the salt is heated in a vacuum, a much lower temperature will suffice to remove the acid and no chloride will be formed. It is necessary to have a neutral product, and for reasons that will appear later, it is impracticable to neutralize by adding silver oxide or carbonate. To make a solution, the silver perchlorate is dissolved in redistilled water and any chloride present is filtered out.

Up to the present our effort has been to compare the results obtained with silver perchlorate as compared with silver nitrate. The two coulometers were of the same pattern as those employed by Professor Guthe at the Bureau of Standards, and the porous cups were made at the same factory and from the same mould. The platinum vessels were ten centimeters in diameter and five cm. deep. When the anode was surrounded with filter paper, the cathode vessels used were eight cm. in diameter. Ten per cent. solutions of both salts were used. The treatment of the deposits has been the usual soaking, heating, and cooling in desiccators. In all the later comparisons the weighings have been made by means of a large and very excellent Rueprecht balance, and the differences have been obtained by balancing one cathode cup against the other.

The results thus far should be stated with reserve because the percentage differences between the nitrate and the perchlorate are very small, and the conclusions derived from one series of determinations are not always sustained by the next one. When the perchlorate of silver is neutralized with pure silver oxide, or is prepared by treating carbonate of silver with perchloride acid, the deposit from the perchlorate is invariably distinctly heavier than that from the nitrate prepared in the usual way. In this respect the perchlorate agrees with the nitrate, since both give a heavier deposit with a solution neutralized with the oxide or the carbonate.

The deposit from the perchlorate differs in appearance from that derived from the nitrate. Whether the anode is in a porous cup, or is enclosed in filter paper, the deposit is always lined or grooved in fine lines running from the bottom of the platinum cup to the top of the solution. The deposit from the nitrate is in more or less detached crystals, which do not adhere together so well as the grooved deposit when the electrolyte is the perchlorate. Hence the weighed washings from the nitrate are usually greater than from the perchlorate.

Two series of comparisons have recently been made, one with the anodes in porous cups, and the other with the anodes wrapped in Baker & Adamson's washed filter paper. In the first series the deposits from the perchlorate average 0.023 per cent. heavier than that from the nitrate. In one case only did the nitrate give a deposit heavier by an insignificant per cent.

In the other series with the filter paper, the deposit from the perchlorate average only 0.013 per cent. heavier, and in half of the series of six determinations the nitrate gave the heavier deposit. Taken all together, the comparisons thus far appear to show a slightly heavier deposit from the perchlorate, and at the same time the indications are that no reduction or other products are formed from the perchlorate and no complex anodic compound is present. We do not thus far find any advantage in using the porous cup; in fact the porous cup is objectionable from several points of view. Ordinary filter paper cannot be used, but the washed paper appears not to be objectionable. Further investigation will be necessary in order to settle this point definitely.

## A Lecture Experiment in Electrolytic Thermo-Electromotive Force.[1]

By Henry S. Carhart.

In the Helmholtz equation for the E.M.F. of a voltaic cell,

$$E = \frac{H}{Q} + T \cdot \frac{dE}{dT},$$

the second term is dependent on the temperature coefficient of the cell, and this coefficient is admittedly due to the thermo-electromotive forces at the several junctions of dissimilar substances in the cell. Whenever, therefore, the conditions are such that the heat of reaction is negligible, the first term, $H/Q$, becomes zero and only the second term remains. Such are approximately at least the conditions in a Helmholtz concentration cell. The E.M.F. of such a cell is thermoelectric in origin and should be represented by the second term of the Helmholtz equation.

A concentration cell with pure silver electrodes and solutions of silver nitrate, whose ratio of concentrations was 5.26, gave an E.M.F. at 30° of 0.0452 volt. The mean of two determinations of the temperature coefficient, $dE/dT$, was 0.000144. Whence $E$, calculated by the expression $T \cdot dE/dT$, is 0.000144 × 303 or 0.0436.

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[1] Abstract of a paper presented at the Ithaca meeting of the Physical Society, June 29–July 3, 1906.

A similar concentration cell with cadmium amalgam and one-tenth and one hundredth normal cadmium sulphate solutions had an E.M.F. at 22.35° C. of 0.034 volt. The mean temperature coefficient was 0.0001085. Whence the calculated value of $E$ is $0.0001085 \times 295.35$ or 0.032. The calculated value in both cases is below the measured E.M.F., indicating that there is a little heat of reaction, due perhaps to mixing the solutions.

From the curve obtained by the author,[1] expressing the relation between the thermo-electromotive forces of Zn — $ZnSO_4$ and the corresponding concentrations of the zinc sulphate solution, the following equation may be derived:

$$dE = a \cdot T \cdot \frac{dC}{C}. \quad \text{Whence } E = a \cdot T \log C.$$

This expression is the potential difference at a single electrode. For two electrodes immersed in solutions of different concentrations, the expression becomes

$$E = a \cdot T \cdot \log \frac{C_2}{C_1}.$$

This equation will be recognized as the one derived by Nernst from the theory of osmotic pressure. The derivative of $E$ with respect to $T$, is

$$\frac{dE}{dT} = a \cdot \log \frac{C}{C}.$$

Solve for the constant $a$, substitute in the above equation for $E$, and we get $E = T \cdot dE/dT$, the second term of the Helmholtz equation. We have thus the nexus between the Helmholtz and the Nernst equations, and at the same time it appears that the latter may be derived from thermo-electric data.

The lecture experiment of the paper is intended to illustrate electrolytic thermo-electromotive force. Two fine iron wires are soldered to the ends of a piece of "constantan" wire as a thermal couple. The junctions are placed in thin glass tubes and a little mercury is poured in to conduct heat. A helix of fine copper wire is wound closely around the end of each tube outside the junction of the iron and constantan. The tubes with their thermal junctions are then immersed in a concentrated solution of copper sulphate, and current is passed through by means of the copper wires. A sufficiently sensitive galvanometer shows that a difference of temperature is soon established between the copper electrodes, the anode, where the current encounters an opposing E.M.F., being the warmer. Heat is generated at the anode and absorbed at the cathode by the thermo-electromotive force.

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[1] Transactions of the American Electrochemical Society, Vol. II., p. 123.

*Volume XXIII. September, 1906. Number 3*

# THE
# PHYSICAL REVIEW.

## THE INFLUENCE OF FREQUENCY UPON THE SELF-INDUCTANCE OF CYLINDRICAL COILS OF *m*-LAYERS.

BY J. G. COFFIN.

IN the construction of an absolute standard of self-inductance for the Bureau of Standards it was found by calculation[1] that a diminution of as much as .3 per cent. in the self-inductance of the coil could take place as the frequency increased from zero to infinity.

This change, which in coils of small radius may be far larger than this, must certainly be allowed for in accurate measurements the precision of which may in certain cases reach as high as 1 in 100,000.[2]

Whether much of this change occurs at low frequencies, or whether it requires high frequencies to produce a large fraction of it, it was not possible to determine. The necessity of finding an answer to the problem suggested above, at least with reference to the calculation of standards of precision, has long been apparent to the writer.

It is true that Max Wien[3] derived an expression for the change in self-inductance of a coil of a single layer, but his results are applicable only to very low frequencies indeed, and the extension of his results, which are in the form of an infinite series, for higher frequencies, even for coils of a single layer, seems very laborious.

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[1] Bull. Bureau Stand. On the Construction and Calculation of Standards of Self-Inductance.

[2] Bull. Bureau Stand., Vol. I., No. 3, Rosa and Grover. Measurements of Self-Inductance.

[3] Ann. d. Physik., 14, p. 1, 1904.

A. Sommerfeld,[1] somewhat later, in a very interesting and original paper has derived an expression in elementary functions for the change in *resistance* of cylindrical coils for all frequencies. It is by means of the method originated by him that we shall be able to derive a finite expression for the change in self-inductance of a cylindrical coil of any number of layers, and valid for all frequencies. The reader is referred to his paper for the details which it was thought best not to reprint on account of length.

## DERIVATION OF THE FORMULÆ.

Consider $m$, co-axial, cylindrical, infinitely long current-sheets, of internal and external radii

$$\begin{array}{ll} r_0 & \text{and } r_1, \\ r_1 & \text{and } r_2, \\ \cdot\ \cdot\ \cdot & \cdot\ \cdot\ \cdot \\ r_{m-1} & \text{and } r_m, \end{array}$$

respectively. We are thus neglecting the thickness of the insulation. Let $r_1 - r_0 = r_2 - r_1 = r_3 - r_2 = \cdots = r_m - r_{m-1} = d$ be the common thickness of these current sheets.

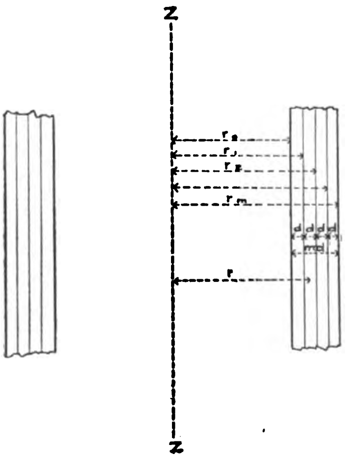

Fig. 1.

Let the symbols $S(\ )$ and $V(\ )$ denote the scalar and vector products respectively. $\nabla(\ )$ is the Hamiltonian operator. $V\nabla(\ )$ is the same as curl ( ) or rot ( ), while $S\nabla(\ )$ is the same as div ( ).

By symmetry, the field inside of the coil is axial, and a function of "$r$" alone, at any given time, and on account of the infinite length of the coil, the field is all inside of the cylinder of radius $r_m$.

In the dielectric, Maxwell's equations are, if we neglect the displacement current,

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[1] Ann. d. Physik., 15, p. 673, 1904.

$$V\nabla H = 0 \quad \text{and} \quad S\nabla H = 0. \tag{1}$$

From the second relation we find that $H$ is independent of $z$, and from the first relation, that it is independent of $x$ and $y$; hence it is constant inside the coil, and for

$$r \overline{\gtrless} r_0 \quad \text{let us assume} \quad H = H_0 e^{i\omega t}, \tag{2}$$

where $\omega$ is $2\pi \times$ frequency, and $H_0$ the maximum value of $H$. This of course means an harmonic alternating field. Outside of the coil, $H$ must be constant, but as it vanishes at infinity it is zero everywhere. Hence for

$$r \overline{\gtrless} r_m, \quad H = 0. \tag{3}$$

In the material of the coil, Maxwell's equations are

$$4\pi q = V\nabla H, \quad \frac{dH}{dt} = -V\nabla F \quad \text{and} \quad q = \sigma F, \tag{4}$$

where $q$ is the current density,
$F$ is the electric force,
$\sigma$ is the specific conductivity,

from which follow

$$S\nabla H = 0 \quad \text{and} \quad S\nabla q = 0. \tag{5}$$

Eliminating $q$ and $F$, by taking the curl of the first equation of (4)

$$4\pi V\nabla q = V\nabla V\nabla H = \nabla S\nabla H - \nabla^2 H$$
$$= -\nabla^2 H \quad \text{by (5)},$$

and from the second and third of (4)

$$V\nabla q = \sigma V\nabla F = -\sigma\frac{dH}{dt},$$

$$\therefore 4\pi\sigma\frac{dH}{dt} = \nabla^2 H. \tag{6}$$

Now assume $H$ in the material of the coil to be given by a function of $r$ alone (on account of symmetry) multiplied by $H_0 e^{i\omega t}$, so that for any point for which $r_0 < r < r_m$,

$$H = H_0 U e^{i\omega t},$$

where
$$U = 1 \quad \text{when} \quad r \overset{=}{<} r_0,$$
$$U = 0 \quad \text{when} \quad r \overset{=}{>} r_m,$$
and $U = f(r)$ for $r_0 < r < r_m$.

In between these points we assume the field to be of the same periodicity but to vary from point to point according to a function of the radius alone. It is also necessary to assume the field continuous as we go from layer to layer.

Equation (6) becomes then in polar coördinates

$$\frac{d^2U}{dr^2} + \frac{1}{r}\frac{dU}{dr} + k^2U = 0, \tag{7}$$

where $k^2 = -i4\pi\sigma\omega$. The solutions of this equation are the Bessel's functions of order zero, $J_0$ and $K_0$, and the complete solution is

$$H = H_0\{AJ_0(kr) + BK_0(kr)\}e^{i\omega t}, \tag{8}$$

where $A$ and $B$ are arbitrary constants. So that for

$$\begin{array}{ll} r < r_0, & H = H_0e^{i\omega t}; \\ r_0 < r < r_1, & H_1 = \{A_1J_0(kr) + B_1K_0(kr)\}H_0e^{i\omega t}; \\ r_1 < r < r_2, & H_2 = \{A_2J_0(kr) + B_2K_0(kr)\}H_0e^{i\omega t}; \\ \cdots & \cdots \\ r_{m-1} < r < r_m, & H_m = \{A_mJ_0(kr) + B_mK_0(kr)\}H_0e^{i\omega t}. \end{array} \tag{9}$$

The $2m$ constants, $A_1, B_1, A_2, B_2, \cdots A_m, B_m$, must be so chosen that, $H$, the field, is continuous from the inside of the coil to the outside. This will give rise to $m$ equations of condition but which are insufficient to determine the $2m$ constants.

The same current, however, flows in each layer, and the current density is given by the equation

$$4\pi q = \text{curl } H = -\frac{dH}{dr}. \tag{10}$$

So that the total current in any layer per unit length of the current sheet, by integration of (10) over the layer in question is given by

$$\begin{aligned} 4\pi NI &= H_1(r_0) - H_1(r_1) = H_2(r_1) - H_2(r_2) = \text{etc.} \\ &= H_m(r_{m-1}) - H_m(r_m), \end{aligned} \tag{11}$$

where $I$ is the current, and $N$ the number of turns per unit length axially, of the coil. Equation (11) means that the magnetic field decreases by equal steps as we pass from layer to layer outwards; as the total decrease is from $H_0e^{i\omega t}$ to 0, and there are $m$ layers, this constant decrease is $H_0e^{i\omega t}/m$.

So that

$$4\pi NI = \frac{1}{m} H_0 e^{i\omega t},$$

or

$$I = \frac{1}{4\pi mN} H_0 e^{i\omega t}. \tag{12}$$

This, which is equivalent to $m$ equations, see equations (11), gives a sufficient number in conjunction with those of (9) to determine the necessary $2m$ constants.

It may be shown[1] that

$$U = \sqrt{\frac{1}{kr}}\, e^{ikr}$$

and

$$U = \sqrt{\frac{1}{kr}}\, e^{-ikr} \tag{13}$$

are very good approximations to the solutions of the differential equation (7) for large values of $kr$, and it may also be shown by expanding them that they are valid for *small* values of $kr$; hence they are very valuable substitutes for the Bessel functions $J_0$ and $K_0$. The problem is thus reduced to the domain of elementary functions. The reader is referred for further particulars on this point to Sommerfeld's Papers on Waves on Wires,[2] and on Increase of Resistance with Frequency[3] in the Annalen.

Employing these functions equations (9) give, remembering equation (12):

$$A_1 e^{ikr_0} + B_1 e^{-ikr_0} = \frac{m-0}{m} \sqrt{kr_0},$$

$$A_1 e^{ikr_1} + B_1 e^{-ikr_1} = \frac{m-1}{m} \sqrt{kr_1},$$

. . . . . . . .

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[1] Wied. Ann., 15, loc. cit.

[2] Wied. Ann., 67, p. 233, 1899.

[3] Ann. d. Phys., 15, p. 678.

$$\begin{aligned} A_2 e^{ikr_1} + B_2 e^{-ikr_1} &= \frac{m-1}{m}\sqrt{kr_1}, \\ A_2 e^{ikr_2} + B_2 e^{-ikr_2} &= \frac{m-2}{m}\sqrt{kr_2}, \\ \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot & \quad \cdot \quad \cdot \quad \cdot \quad \cdot \\ A_m e^{ikr_{m-1}} + B_m e^{-ikr_{m-1}} &= \frac{m-(m-1)}{m}\sqrt{kr_{m-1}}, \\ A_m e^{ikr_m} + B_m e^{-ikr_m} &= \frac{m-m}{m}\sqrt{kr_m}. \end{aligned} \tag{14}$$

Consider equations in $A_2$ and $B_2$ of equations (14).

Multiply the first by $e^{-ikr_2}$ and the second by $e^{-ikr_1}$ and subtract. This gives

$$A_2 e^{-ik(r_2-r_1)} + B_2 e^{-ik(r_1+r_2)} = \frac{m-1}{m}\sqrt{kr_1}\,e^{-ikr_2},$$

$$A_2 e^{+ik(r_2-r_1)} + B_2 e^{-ik(r_1+r_2)} = \frac{m-2}{m}\sqrt{kr_2}\,e^{-ikr_1},$$

$$A_2\left(e^{-ik(r_2-r_1)} - e^{ik(r_2-r_1)}\right) = \frac{m-1}{m}\sqrt{kr_1}\,e^{-ikr_2} - \frac{m-2}{m}\sqrt{kr_2}\,e^{-ikr_1},$$

$$\therefore A_2 = \frac{-\frac{m-1}{m}\sqrt{kr_1}\,e^{-ikr_2} + \frac{m-2}{m}\sqrt{kr_2}\,e^{-ikr_1}}{e^{ik(r_2-r_1)} - e^{-ik(r_2-r_1)}}. \tag{15}$$

In a similar way, multiplying the first equation by $e^{ikr_2}$ and the second by $e^{ikr_1}$ and subtracting we obtain for $B_2$

$$B_2 = \frac{\frac{m-1}{m}\sqrt{kr_1}\,e^{ikr_2} - \frac{m-2}{m}\sqrt{kr_2}\,e^{ikr_1}}{e^{ik(r_2-r_1)} - e^{-ik(r_2-r_1)}}. \tag{16}$$

The others are formed in an analogous manner. Hence

$$H_2 = \left\{A_2 \frac{1}{\sqrt{kr}} e^{ikr} + B_2 \frac{1}{\sqrt{kr}} e^{-ikr}\right\} H_0 e^{i\omega t},$$

$$H_2 = \left\{\frac{m-1}{m}\sqrt{\frac{r_1}{r}}\,\frac{e^{ik(r_2-r)} - e^{-ik(r_2-r)}}{e^{ik(r_2-r_1)} - e^{-ik(r_2-r_1)}} - \frac{m-2}{m}\sqrt{\frac{r_2}{r}}\,\frac{e^{ik(r_1-r)} - e^{-ik(r_1-r)}}{e^{ik(r_2-r_1)} - e^{-ik(r_2-r_1)}}\right\} H_0 e^{i\omega t} \tag{17}$$

$$=\left\{\frac{m-1}{m}\sqrt{\frac{r_1}{r}}\,\frac{\sin k(r_2-r)}{\sin k(r_2-r_1)}-\frac{m-2}{m}\sqrt{\frac{r_2}{r}}\,\frac{\sin k(r_1-r)}{\sin k(r_2-r_1)}\right\}H_0e^{i\omega t}. \qquad (18)$$

Call

$$r_0-r=d_0,\qquad r_1-r=d_1\cdots\text{etc.}$$

$$r_2-r_1=r_3-r_2=r_S-r_{S-1}=d,$$

and put $k=h-i$.

Then equation (18) becomes

$$H_2=\left\{\frac{m-1}{m}\sqrt{\frac{r_1}{r}}\,\frac{\sin(d_2-id_2)h}{\sin(d-id)h}\right.$$

$$\left.-\frac{m-2}{m}\sqrt{\frac{r_2}{r}}\,\frac{\sin(d_1-id_1)h}{\sin(d-id)h}\right\}H_0e^{i\omega t}. \qquad (19)$$

The conjugate of this obtained by putting $-i$ for $i$ everywhere in equation (19) is

$$\bar{H}_2=\left\{\frac{m-1}{m}\sqrt{\frac{r_1}{r}}\,\frac{\sin(d_2+id_2)h}{\sin(d+id)h}\right.$$

$$\left.-\frac{m-2}{m}\sqrt{\frac{r_2}{r}}\,\frac{\sin(d_1+id_1)h}{\sin(d+id)h}\right\}H_0e^{-i\omega t}, \qquad (20)$$

where the dash over a letter denotes the conjugate expression for it.

The electro-magnetic energy of a system is in general:

$$T=\tfrac{1}{2}LI^2,$$

or in this case

$$\tilde{T}=\tfrac{1}{2}L\tilde{I}^2,$$

where

$L=$ self-inductance of the system,

$I=$ current in it, (21)

$T=$ electro-magnetic energy,

and where the sign ~ over a variable denotes its mean square value. Whence

$$L=\frac{2\tilde{T}}{\tilde{I}^2}=2\cdot\frac{\dfrac{1}{\tau}\displaystyle\int_0^\tau T\,dt}{\dfrac{1}{\tau}\displaystyle\int_0^\tau I^2\,dt}.$$

To obtain the mean square value of a variable $I$ it is necessary to evaluate the integral

$$\frac{1}{\tau}\int_0^\tau I^2 dt,$$

where $\tau$ is the time of a period. For sine or cosine functions we know that $\tilde{I}^2 = \frac{1}{2}$ the square of the maximum value of $I$. But the square of the amplitude of any *imaginary* expression is obtained by multiplying the expression by its conjugate; hence to obtain the mean square value of any function, in imaginaries, of this paper we multiply it by its conjugate and divide it by 2. So that

$$\frac{1}{\tau}\int_0^\tau I^2 dt = \frac{1}{2}|I|^2 = \frac{1}{2}I\bar{I} = \frac{1}{2}\frac{1}{4\pi mN}H_0 e^{i\omega t} \times \frac{1}{4\pi mN}e^{-i\omega t}$$

$$= \frac{1}{2}\left(\frac{H_0}{4\pi mN}\right)^2 = \frac{1}{2}\frac{H_0^2}{J^2} \quad \text{where} \quad J = 4\pi mN. \qquad (22)$$

Hence (21) becomes

$$L = \frac{2\tilde{T}}{\frac{1}{2}\frac{H_0^2}{J^2}} = 4\frac{J^2}{H_0^2}\frac{1}{\tau}\int_0^\tau T dt. \qquad (23)$$

But

$$T = \frac{1}{8\pi}\iiint H^2 dv = \frac{1}{8\pi}\int_0^{2\pi} d\varphi \int H^2 r dr = \frac{1}{4}\int_{r=0}^{r=\infty} H^2 r dr \qquad (24)$$

per unit length of the coil.

$$\therefore L = \frac{J^2}{H_0^2}\left\{\frac{1}{\tau}\int_0^\tau dt \int_0^\infty H^2 r dr\right\} = \frac{J^2}{H_0^2}\int_0^\infty r dr \frac{1}{\tau}\int_0^\tau H^2 dt$$

$$= \frac{J^2}{2H_0^2}\int_0^\infty H\bar{H} r dr$$

$$= \frac{J^2}{2H_0^2}\left\{\int_0^{r_0} H\bar{H} r dr + \int_{r_0}^{r_1} H\bar{H} r dr + \int_{r_1}^{r_2} H\bar{H} r dr + \cdots + \int_{r_{m-1}}^{r_m} H\bar{H} r dr\right\}, \qquad (25)$$

$$= \frac{J^2}{2H_0^2}\{T_0 + T_1 + T_2 + \cdots + T_m\}, \qquad (26)$$

$$T_0 = \int_0^{r_0} r dr H_0 e^{i\omega t} H_0 e^{-i\omega t} = \int_0^{r_0} r dr H_0^2 = \frac{H_0^2}{2} r_0^2. \qquad (27)$$

Let us find an expression for $H_2\bar{H}_2$ by multiplying together equations (19) and (20).

$$H_2\bar{H}_2 = \Bigg[\left(\frac{m-1}{m}\right)^2 \frac{r_1}{r}\,\frac{\sin(hd_2 - ihd_2)\sin(hd_2 + ihd_2)}{\sin(hd - ihd)\sin(hd + ihd)} + \left(\frac{m-2}{m}\right)^2 \frac{r_2}{r}$$

$$\times \frac{\sin(hd_1 - ihd_1)\sin(hd_1 + ihd_1)}{\sin(hd - ihd)\sin(hd + ihd)} - \left(\frac{m-1}{m}\right)\left(\frac{m-2}{m}\right)\sqrt{\frac{r_1 r_2}{rr}} \qquad (28)$$

$$\times \frac{\sin(hd_1 + ihd_1)\sin(hd_2 - ihd_2) + \sin(hd_1 - ihd_1)\sin(hd_2 + ihd_2)}{\sin(hd - ihd)\sin(hd + ihd)}\Bigg] \times H_0^2.$$

Expression (28) may be reduced by means of the following formulæ:

$$\sin(a_1 + ia_1)\sin(a_2 - ia_2) + \sin(a_1 - ia_1)\sin(a_2 + ia_2)$$

$$= \cos(a_1 - a_2)\cos i(a_1 + a_2) - \cos(a_1 + a_2)\cos i(a_1 - a_2) \qquad (29)$$

$$= \cos(a_1 - a_2)\cosh(a_1 + a_2) - \cos(a_1 + a_2)\cosh(a_1 - a_2)$$

and

$$\sin(a - ia)\sin(a + ia) = \tfrac{1}{2}\cos 2ia - \tfrac{1}{2}\cos 2a$$

$$= \frac{\cosh 2a - \cos 2a}{2} \qquad (30)$$

to

$$H_2\bar{H}_2 = \Bigg[\left(\frac{m-1}{m}\right)^2 \frac{r_1}{r}\,\frac{\cosh 2hd_2 - \cos 2hd_2}{\cosh 2hd - \cos 2hd} + \left(\frac{m+1}{m}\right)^2 \frac{r_2}{r}$$

$$\times \frac{\cosh 2hd_1 - \cosh 2hd_1}{\cosh 2hd - \cos 2hd} - 2\left(\frac{m-1}{m}\right)\left(\frac{m-2}{m}\right)\sqrt{\frac{r_1 r_2}{rr}} \qquad (31)$$

$$\times \frac{\cosh(d_2 + d_1)h\cos(d_2 - d_1)h - \cosh(d_2 - d_1)h\cos(d_2 + d_1)h}{\cosh 2hd - \cos 2hd}\Bigg] H_0^2.$$

This transformation may also be accomplished by substituting $h - i$ for $k$ in equation (17), forming the conjugate, multiplying out, and remembering that

$$\cos y = \frac{e^{iy} + e^{-iy}}{2}$$

and that

$$\cosh y = \frac{e^{y} + e^{-y}}{2}, \text{ etc.}$$

It is now necessary to integrate this expression multiplied by $rdr$

from $r_1$ to $r_2$. For example

$$\int_{r_1}^{r_2}\frac{1}{r}\cosh 2h(r_2-r)rdr=-\frac{1}{2h}\int_{r_1}^{r_2}\cosh 2h(r_2-r)(-2hdr)$$

$$=-\frac{1}{2h}\Big[\sinh 2h(r_2-r_2)-\sinh 2h(r_2-r_1)\Big]=\frac{1}{2h}\sinh 2hd. \quad (32)$$

And

$$\int_{r_1}^{r_2}\frac{1}{r}\cosh 2h\left(\frac{r_1+r_2}{2}-r\right)rdr$$

$$=-\frac{1}{2h}\int_{r_1}^{r_2}\cosh 2h\left(\frac{r_1+r_2}{2}-r\right)(-2hdr)$$

$$=-\frac{1}{2h}\left[\sinh 2h\left(\frac{r_1+r_2}{2}-r_2\right)-\sinh 2h\left(\frac{r_1+r_2}{2}-r_1\right)\right]$$

$$=-\frac{1}{2h}\left[\sinh h(r_1-r_2)-\sinh h(r_2-r_1)\right]$$

$$=\frac{1}{h}\sinh h(r_2-r_1)=\frac{1}{h}\sinh hd, \text{ etc.} \quad (33)$$

Carrying out these integrations and putting $x=2hd$ the integrated expression simplifies into

$$\int_{r_1}^{r_2}H_2\bar{H}_2rdr=\Bigg[\left\{\left(\frac{m-1}{m}\right)^2\frac{r_1d}{3}+\left(\frac{m-2}{m}\right)\frac{r_2d}{3}\right\}\left\{\frac{3}{x}\frac{\sinh x-\sin x}{\cosh x-\cos x}\right\}$$

$$+\left\{\left(\frac{m-1}{m}\right)\left(\frac{m-2}{m}\right)\frac{d\sqrt{r_1r_2}}{3}\right\}\left\{\frac{12}{x}\frac{\cosh\frac{1}{2}x\sin\frac{1}{2}x-\sinh\frac{1}{2}x\cos\frac{1}{2}x}{\cosh\frac{1}{2}x\cosh\frac{1}{2}x-\cos\frac{1}{2}x\cos\frac{1}{2}x}\right\}\Bigg]H_0^2. \quad (34)$$

Remembering equation (25) and substituting in it equations (27) and (34) we obtain

$$L_\omega=\frac{J^2}{4}\left\{r_0^2+\frac{2}{3}\frac{d}{m^2}(Q'P'+Q''P'')\right\}, \quad (35)$$

where

$$Q'=\frac{3}{x}\frac{\sinh x-\sin x}{\cosh x-\cos x} \quad\text{and}\quad \begin{array}{l}Q'=1 \text{ when } x=0,\\ Q'=0 \text{ when } x=\infty,\end{array} \quad (36)$$

where

$$Q'' = \frac{12}{x}\frac{\cosh x/2 \sin x/2 - \sinh x/2 \cos x/2}{\cosh x/2 \cosh x/2 - \cos x/2 \cos x/2} \tag{37}$$

and $Q'' = 1$ when $x = 0$, $Q'' = 0$ when $x = \infty$,
where

$$P' = m^2r_0 + 2(m-1)^2r_1 + 2(m-2)^2r_2 + 2(m-3)^2r_3 + 2r_{m-1} \tag{38}$$

and where

$$P'' = m(m-1)\sqrt{r_0r_1} + (m-1)(m-2)\sqrt{r_1r_2} \\ + [m-(m-2)][m-(m-1)]\sqrt{r_{m-2}r_{m-1}}. \tag{39}$$

Since for $x = \infty$ equation (36) becomes

$$L_\infty = \frac{J^2}{4}r_0^2 = 4\pi^2m^2N^2r_0^2 \tag{40}$$

we may write it

$$\frac{L_\omega - L_\infty}{L_\infty} = \frac{2}{3}\frac{d}{rm_0^2}(Q'P' + Q''P'') \tag{41}$$

Equation (40) gives the curious result that for infinite frequency the self-inductance of a coil of *m*-layers, and consequntly having *md* units of thickness of winding, diminishes to what it would be were the total current all flowing at distance *r*. That is, it diminishes in *absolute* amount as much as if it were a single layer, *md* units thick. But of course the self-inductance of *m*-layers being approximately $m^2$ times that of a single layer, the total *fractional* change is *m* times less in amount.

This result may be explained by a consideration of the following equations taken from Sommerfeld's[1] paper and previously explained by Wien,[2] which give the value of the current density at the bounding surfaces of the layers, where for infinite frequency it is mostly concentrated.

$$\begin{aligned} \text{For } r = r_0, \quad & 4\pi q_1 = ikH_0e^{i\omega t}; \\ r = r_1, \quad & -4\pi q_1 = 4\pi q_2 = ik\frac{m-1}{m}H_0e^{i\omega t}; \\ r = r_2, \quad & -4\pi q_2 = 4\pi q_3 = ik\frac{m-2}{m}H_0e^{i\omega t}. \end{aligned} \tag{42}$$

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[1] Ann. d. Phys., 15; loc. cit., p. 698.

[2] Ann. d. Phys., 14; loc. cit., p. 9.

It is here seen that the current decreases $1/m^{\text{th}}$ in amplitude as we go from one layer to the next, and that at the bounding surfaces of the layers the currents are *equal* in amount, but *opposite* in phase, so that in the material of the wire there is current, but no magnetic field.

For $x = 0$ (41) becomes

$$\frac{L_0 - L_\infty}{L_\infty} = \tfrac{2}{3}\frac{d}{r_0^2 m^2}(P' + P''). \tag{43}$$

This is then the total possible fractional change.

If $m = 1$, $P' = r_0$ and $P'' = 0$, (42) becoming

$$\frac{L_\omega - L_\infty}{L_\infty} = \tfrac{2}{3}\frac{d}{r_0}Q'$$

for a coil of a single layer. Dividing (41) by (43) we obtain

$$\frac{L_\omega - L_\infty}{L_0 - L_\infty} = \frac{Q'P' + Q''P''}{P' + P''} \qquad (44$$

which represents the fraction of the total possible change still to take place at frequency $\omega$ where $\omega = 2\pi n$ and $n =$ number of alternations per second,

$$= \tfrac{1}{2}(Q' + Q'') + \tfrac{1}{2}\frac{P' - P''}{P' + P''}(Q' - Q'')$$

$$= \tfrac{1}{2}(Q' + Q'') + P\tfrac{1}{2}(Q' - Q'') \tag{45}$$

where

$$P = \frac{P' - P''}{P' + P''}$$

and $P = 1$ when $m = 1$.

To facilitate computation the two functions $Q'$ and $Q''$ have been carefully calculated and plotted for different values of

$$x = 2hd = 2d\sqrt{2\pi\omega\sigma} = (4\pi d\sqrt{\sigma})\sqrt{n}. \tag{46}$$

In Table I. are the data used in the computation.

The mathematical tables of Vladimir Vassal were employed in finding the values of cosh $x$ and of sinh $x$ for different values of $x$.

Equations (38) and (39) give for different values of $m$, remembering that $r_n = r_0 + nd$, where $d$ is the thickness of the wire.

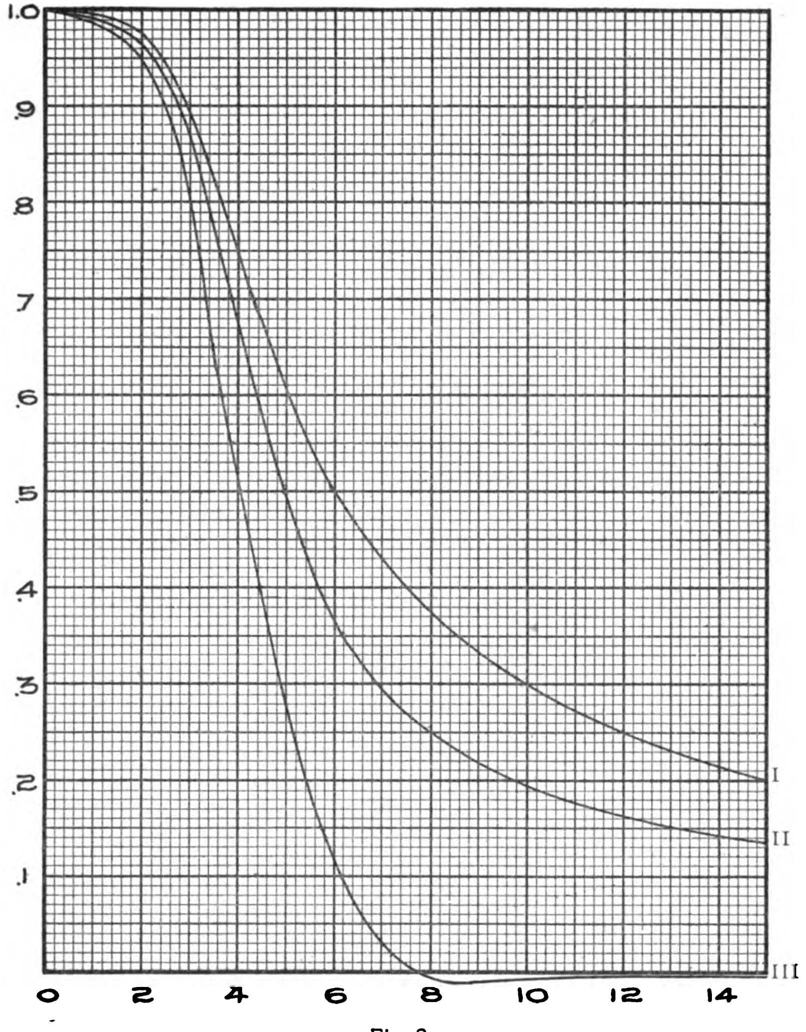

Fig. 2.

I (upper curve) is $Q'$; II (middle curve) is $Q' - \frac{1}{3}(Q' - Q'')$;
III (lower curve) is $Q''$.

And assuming in (39) that $\sqrt{r_{m-1}r_m} = \frac{1}{2}(r_{m-1}+r_m)$, which is always very approximately true, as $r_{m-1}$ and $r_m$ have but slightly different values.

## TABLE I.

*Values for the Computation of the Functions $Q'$ and $Q''$.*

| $x$ | cosh $x$ | sinh $x$ | cos $x$ | sin $x$ | $\theta$ | $Q'$ | $Q''$ |
|---|---|---|---|---|---|---|---|
| 0.00 | 1.0000 | 0.0000 | 1.0000 | 0.0000 | 0.00 | 1.0000 | 1.000 |
| 0.25 | 1.0314 | 0.2526 | 0.9689 | 0.2473 | 14.32 | —— | |
| 0.50 | 1.1276 | 0.5211 | 0.8776 | 0.4789 | 28.65 | 0.9999 | 0.993 |
| 1.00 | 1.5431 | 1.1752 | 0.5402 | 0.8415 | 57.30 | 0.9984 | 0.992 |
| 1.50 | 2.3523 | 2.1291 | 0.0706 | 0.9975 | —— | 0.9920 | |
| 1.75 | 2.964 | 2.790 | —0.1788 | 0.9839 | 100.3 | —— | |
| 2.00 | 3.7622 | 3.6269 | —0.4163 | 0.9092 | —— | 0.9756 | 0.951 |
| 2.50 | 6.133 | 6.051 | —0.8018 | 0.5990 | 143.2 | —— | |
| 3.00 | 10.0677 | 10.0178 | —0.9900 | 0.1490 | —— | 0.8932 | |
| 3.50 | 16.578 | 16.547 | —0.9348 | —0.3551 | 171.9 | —— | 0.793 |
| 3.60 | 18.30 | 18.28 | —— | —— | —— | —— | 0.667 |
| 3.65 | 19.244 | 19.218 | —0.8738 | —0.4863 | 209.1 | —— | |
| 3.80 | 22.33 | 22.31 | —0.7902 | —0.6129 | —— | —— | |
| 3.90 | 24.72 | 24.70 | —0.7218 | —0.6921 | 217.8 | —— | |
| 4.00 | 27.308 | 27.262 | —0.6534 | —0.7570 | —— | 0.7515 | 0.529 |
| 4.50 | 45.23 | 45.22 | —0.2096 | —0.9778 | 257.9 | —— | |
| 5.00 | 74.204 | 74.197 | +0.2840 | —0.9588 | —— | 0.6100 | 0.276 |
| 6.00 | 201.8 | 201.8 | 0.9537 | —0.3007 | 343.5 | 0.5032 | 0.1202 |
| 7.00 | 547.8 | 547.8 | 0.7537 | +0.6574 | —— | 0.4287 | 0.0299 |
| 7.30 | 740 | 740 | —— | —— | —— | —— | 0.0165 |
| 7.60 | 997 | 997 | —— | —— | —— | —— | 0.00631 |
| 7.80 | 1,224 | 1,224 | —— | —— | —— | —— | 0.00088 |
| 8.00 | 1,490 | 1,490 | —0.1461 | +0.989 | 458.4 | 0.3750 | —0.0029 |
| 9.00 | 4,080 | 4,080 | —— | —— | —— | 0.3333 | —0.0113 |
| 10.00 | 11,000 | 11,000 | —0.839 | —0.545 | 573 | 0.3000 | —0.010 |
| 12.00 | 81,400 | 81,400 | —— | —— | —— | 0.2500 | —0.0062 |
| 16.00 | 4,440,000 | 4,440,000 | —0.9563 | —0.293 | 917 | 0.1875 | —0.0003 |
| ∞ | ∞ | ∞ | Indet. | Indet. | ∞ | 0.0000 | 0.0 |

| $m$ | $P'$ | $P''$ | $m$ | $P'$ | $P''$ |
|---|---|---|---|---|---|
| 1 | $r_0$ | 0 | 5 | $85r_0 + 100d$ | $40r_0 + 50d$ |
| 2 | $6r_0 + 2d$ | $2r_0 + d$ | 6 | $146r_0 + 210d$ | $70r_0 + 105d$ |
| 3 | $19r_0 + 12d$ | $8r_0 + 6d$ | etc. | .............. | .............. |
| 4 | $44r_0 + 40d$ | $20r_0 + 20d$ | | . | |

One easily notices that

$$P' = 2P'' + mr_0. \tag{47}$$

So that

$$P = \frac{P' - P''}{P' + P''} = \frac{P'' + mr_0}{3P'' + mr_0}. \tag{48}$$

It may be shown by the method of differences that the coefficients of $r_0$ and $d$ in $P'$ are given in general by

$$\rho_m = 2(m-1) + 2(m-1)(m-2) + \frac{(m-1)(m-2)(m-3)}{3} \qquad (49)$$

and

$$\delta_m = (m-1) + 2(m-1)(m-2) + \tfrac{5}{8}(m-1)(m-2)(m-3)$$
$$+ \tfrac{1}{12}(m-1)(m-2)(m-3)(m-4). \qquad (50)$$

So that

$$P = \tfrac{1}{3}\,\frac{\left(\rho_m + \delta_m \frac{d}{r_0}\right) + m}{\left(\rho_m + \delta_m \frac{d}{r_0}\right) + m}. \qquad (51)$$

For $m = 1$ this expression is 1 and for $m$ large it approaches $\frac{1}{3}$, so that the function of equation (44) may be written more conveniently

$$\frac{L_\omega - L_\infty}{L_0 - L_\infty} = Q' - (1 - P)\tfrac{1}{2}(Q' - Q''), \qquad (52)$$

which gives the law according to which the fractional change in inductance takes place, and which varies for $m = 1$ and $m$ large from $Q'$ to $Q' - \frac{1}{3}(Q' - Q'')$.

The curves $Q'$ and $Q' - \frac{1}{3}(Q' - Q'')$ are inserted in the plot. Hence all the curves which show the law of falling off of self-inductance in coils of any number of layers, lie in the region between Curves I. and II., and as is easily seen, are of nearly the same shape.

Having thus the two curves $Q'$ and $Q''$ it is easy to construct the characteristic curve for the coil in question and then to derive a calibration table from it.

To obtain the characteristic curve it is necessary to calculate the value of $P$ for a given $m$, $r$ and $d$. Having done this subtract from the ordinates of $Q'$, $(1 - P)$ times the vertical distance between the curves $Q'$ and $Q''$; this amounts to dividing the vertical space between the two curves in the ratio $1 - P$ to 1. The curve drawn through the points, thus derived, will be the curve showing the way in which the self-inductance of that particular coil falls off.

From this curve it is now necessary to derive a second one, by the following process: $x = \{4\pi d\sqrt{\sigma}\}\sqrt{n}$ is the relation between $x$ and $n$ for a coil wound with wire of conductivity $\sigma$, and of diameter $d$, so that every value of $x$ corresponds to a definite frequency. By assuming values of $n$ differing by equal intervals and plotting against these the values of the ordinates above the $x$'s corresponding to the $n$'s, a correction curve is derived for the coil for any frequency.

### Approximations for Low and High Frequencies.

For very small frequencies an expression for (52) much more convenient for calculation may be derived by expanding the cosh $x/2$, sinh $x/2$, cos $x/2$, sin $x/2$, cosh $x$, and cos $x$ by means of their expansions:

$$\cosh x = 1 + \frac{x^2}{2!} + \frac{x^4}{4!} + \cdots; \quad \cos x = 1 - \frac{x^2}{2!} + \frac{x^4}{4!} - \cdots;$$

$$\sinh x = x + \frac{x^3}{3!} + \frac{x^5}{5!} + \cdots; \quad \sin x = x - \frac{x^3}{3!} + \frac{x^5}{5!} - \cdots;$$

and neglecting powers of $x$ higher than the fourth. It was found convenient to employ the formula:

$$\cosh\frac{x}{2}\sin\frac{x}{2} - \sinh\frac{x}{2}\cos\frac{x}{2} = \frac{1+i}{2}\sin\frac{1+i}{2}x + \frac{1-i}{2}\sin\frac{1-i}{2}x$$

$$= \frac{a}{2}\sin\frac{ax}{2} + \frac{b}{2}\sin\frac{bx}{2}, \text{ say.}$$

$$= \frac{a}{2}\left(\frac{ax}{2} - \frac{a^3x^3}{3!\,2^3} + \frac{a^5x^5}{5!\,2^5} - \cdots\right) + \frac{b}{2}\left(\frac{bx}{2} - \frac{b^3x^3}{3!\,2^3} + \frac{b^5x^5}{5!\,2^5} - \cdots\right)$$

$$= x\frac{(a^2+b^2)}{2^2} - \frac{x^3}{3!}\left(\frac{a^4+b^4}{2^4}\right) + \frac{x^5}{5!}\left(\frac{a^6+b^6}{2^6}\right) - \frac{x^7}{7!}\left(\frac{a^8+b^8}{2^8}\right) + \cdots.$$

But since

$$a = 1+i, \quad a^2 = 2i, \quad a^4 = -4, \quad a^6 = -8i, \quad a^8 = 16$$

$$b = 1-i, \quad b^2 = -2i, \quad b^4 = -4, \quad b^6 = +8i, \quad b^8 = 16,$$

this becomes:

$$= \frac{x^3}{3!}\frac{8}{2^4} - \frac{x^7}{7!}\frac{32}{2^8},$$

$$\cosh x - \cos x = 2\left(\frac{x^2}{3!} + \frac{x^6}{6!} + \frac{x^{10}}{10!}\right),$$

$$Q'' = 6\,\frac{\left(\frac{1}{3!}\,\frac{8}{2^4} - \frac{x^4}{7!}\,\frac{32}{2^8}\right)}{\left(\frac{1}{2!} + \frac{x^4}{6!}\right)} = \frac{1 - \frac{3}{2}\,\frac{1}{7!}\,x^4}{1 + \frac{2x^4}{6!}} = \left(1 - \frac{31}{2}\,\frac{x^4}{7!}\right),$$

$$Q' = 3\,\frac{\left(\frac{1}{3!} + \frac{x^4}{7!}\right)}{\left(\frac{1}{2!} + \frac{x^4}{6!}\right)} = \frac{1 + \frac{6x^4}{7!}}{1 + \frac{2x^4}{6!}} = \left(1 - \frac{8x^4}{7!}\right),$$

$$Q' - Q'' = \frac{\frac{15}{2}\,\frac{x^4}{7!}}{1 + \frac{2x^4}{6!}}.$$

By means of these approximations equation (52) may be written

$$\frac{L_\omega - L_\infty}{L_0 - L_\infty} = 1 - \frac{8x^4}{7!}\left[1 + (1 - P)\right]. \tag{53}$$

$(1 - P)/2$ varies from zero to $\frac{1}{3}$, so that the two limiting approximation curves are $1 - 8x^4/7!$ and $1 - \frac{4}{3}\,8x^4 7!$, for small values of $x$. ($x < 2$.)

For high frequencies, which correspond to large values of $x$, we may put $Q'' = 0$; as a consideration of the function shows that it is practically zero for $x > 8$.

Doing this, equation (52) becomes

$$\frac{L_\omega - L_\infty}{L_0 - L_\infty} = \frac{3}{2x}(1 + P). \tag{54}$$

For a coil of a single layer, for which $P = 1$, this becomes $3/x$, so Curve I. beyond abscissæ greater than $x = 7$ is *very* approximately a hyperbola. It is easily seen that all the intermediate curves are also hyperbolæ for $x > 7$.

## SUMMARY.

Following a method analogous to that of A. Sommerfeld, an expression is found giving the change of self-inductance with the frequency, of a long cylindrical coil of any number of layers.

Calling $\lambda$ the fraction of the total possible change, still unchanged at frequency $m = 2\pi n$, where $n =$ number of alternations per sec., the expression obtained may be written

$$\lambda = \frac{L_\omega - L_\infty}{L_0 - L_\infty} = Q' - \tfrac{1}{2}(1 - P)(Q' - Q''),$$

where

$$Q' = \frac{3}{x}\,\frac{\sinh x - \sin x}{\cosh x - \cos x} \quad \text{and} \quad \begin{matrix} Q' = 1 \text{ when } x = 0 \\ Q' = 0 \text{ when } x = \infty \end{matrix},$$

where

$$Q'' = \frac{12}{x}\,\frac{\cosh x/2 \sin x/2 - \sinh x/2 \cos x/2}{\cosh x/2 \cosh x/2 - \cos x/2 \cos x/2} \text{ and } \begin{matrix} Q''=1 \text{ when } x=0 \\ Q''=0 \text{ when } x=\infty \end{matrix},$$

and where $P$ is a function of the dimensions of the coil alone, and which varies from 1 to $\frac{1}{8}$ for $m = 1$ and $m$ large, respectively. See equation 51.

Since a coil of a single layer is of particular interest, the formulæ for this case, which are much less complex than the above, will be given.

For $m = 1$, $P = 1$.

Then

$$\lambda = \frac{3}{x}\,\frac{\sinh x - \sin x}{\cosh x - \cos x}.$$

For small values of $x$ ($x < 2$) this may be written

$$\lambda = 1 - \frac{8x^4}{7!}$$

and for large values of $x$ ($x > 7$)

$$\lambda = \frac{3}{x}.$$

These values agree perfectly with the results, deduced solely for a coil of a single layer, published in the Bulletin of the Bureau of Standards and in the Proc. A. A. A. S., Vol. 41, No. 34, 1906.

Since $4\pi^2 N^2 r_0^2$ is the self-inductance of a coil of a single layer of mean diameter $r_0$, the calculations show (see equation 40) that with increasing frequency, the mean radius of a coil of a single layer decreases by the radius of the wire, with which it is wound. This gives a means of calculating the total possible change in self-inductance.

Equation 40 also shows that the mean radius of a coil of $m$ layers, decreases to the minimum radius $r_0$ of the coil, just as if it were of a single layer wound with wire $md$ units thick. The fractional change in self-inductance, however, is far less than for a coil of one layer, as the self-inductance is approximately $m^2$ greater.

By means of a plot of the functions $Q'$ and $Q''$, the characteristic curve for any given cylindrical coil may be readily calculated and a table of corrections derived for the self inductance at any frequency.

CLARK UNIVERSITY,
March, 1906.

# ON THE VELOCITY OF SOUND IN GASES, AND THE RATIO OF THE SPECIFIC HEATS, AT THE TEMPERATURE OF LIQUID AIR.

By S. R. Cook.

*Historical.* — The determination of the velocity of sound, at temperatures lower than that obtainable in free space, has been made possible within the past few years by the production, in sufficient quantities, of liquid air and other refrigerating fluids. When the present work was planned (summer of 1903) no measurements had been published on the velocity of sound at the temperature of liquid air; and it was not until the work was well under way that my attention was called to a paper on the velocity of sound in nitrogen, which had just appeared in the "Annalen der Physik."[1] The author had used a method similar to that which I had planned; but, as so little work had been done in this particular field, it was considered of sufficient importance to continue the investigation, using gases other than nitrogen.

Greely,[2] during his expedition to the far north, made a great number of determinations of the velocity of sound in free air, by the eye-and-ear-method, over accurately measured courses. The determinations were made attemperatures ranging from 0° F. to —79° F., and it was found that within this range the decrease in the velocity of sound was 60.3 cm. per degree while the ratio of the two specific heats was constant within the accuracy of the measurements.

*Ratio of the Specific Heats.* — A. W. Witkowski[3] and A. Léduc[4] have recently been investigating the specific heats of gases, and have found that there appears to be a variation with both pressure and temperature. The variation with temperature seems very slight, while that with pressure is as great as 10 per cent. at 100 atmospheres. E. H. Stevens,[1] by means of a heated resonance tube, has measured the velocity of sound at temperatures 950° and 1000°, and finds the ratio of the specific heats to be 1.34 for air; while A. Kalahne,[2] by an acoustic method, studied the variation of the ratio of the specific heats from 0° to 900° and finds that the ratio of the specific heats does not vary up to 450°. At 700° it has fallen four parts in one thousand, and at 900° the ratio is 1.39 for air.

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[1] S. Valentiner, Ann. der Physik, Drude 15, pp. 74–106, 1904.

[2] Greely. Meterolog. Zeitschrift, VII., p. 6, 1890; Phil. Mag. (5), 30, 1890.

[3] Witkowski, Acad. Sci. Cracovie Bull., 16, pp. 138–157, 1899.

[4] Léduc, Annal. Chim. Phys., 17, pp. 484–510, 1899.

From the variation of these experimental results, it would seem that the data were still lacking for the establishment of the dependence of the ratio of the specific heats upon temperature. The results obtained for the dependence of the ratio of the specific heats upon pressure show, in general, a decrease both for increase and decrease of pressure, with the greatest variation at the temperature − 136°.

L. Lohncke[3] has studied the variation of the specific heats of the vapor of mercury, and finds no variation with temperature. As the ratio of the specific heats is indirectly a measure of the ratio of translational to the internal energies of the molecules of the gas, and as the vapor of mercury is known to be monatomic, this result might have been expected. It is not so easy, however, to predict the division of energy in a diatomic or polyatomic molecule, with wide ranges of temperature and pressure conditions. Capstick[4] has shown that for a number of organic compounds the ratio of the specific heats of the vapors and therefore the ratio of the translational to the internal energy of molecules of.polyatomic vapors, depends on the number of atoms in the molecule, and is independent of the specific gravity of the vapor.

It was thought that, if there were any variation in the ratio of the specific heats, and therefore in the division of energy between the translational and intermolecular energies of the molecules of the diatomic gases, it would be most likely to occur when these gases were in their vapor condition, or very close to the point of condensation. It was determined, therefore, to study atmosphere air and

[1] Stevens, Deutsche Phys. Gesell. Verh., 3, 5, pp. 54–56, 1901.

[2] Kalahne, Ann. d. Physik., 112, pp. 225–256, 1903.

[3] Lohncke, Wied. Ann., 66 (1), pp. 111–115, 1898.

[4] Capstick, Phil. Trans., 185A, p. 1, 1894; 186A, p, 567, 1895.

oxygen. The critical pressure for air being somewhat greater, and that for oxygen somewhat less than atmospheric pressure at the temperature of liquid air.

From the well known work of Regnault, who determined the specific heat at constant pressure of air, hydrogen, carbon dioxide, and other gases and vapors, from 0° to 200° at pressures between 1 and 12 atmospheres, it has been concluded that for the so-called permanent gases the specific heats do not vary with temperature or pressure, but for the more compressible gases and vapors a small variation is quite probable.

For an ideal gas, in which the influence of the forces due to the mass of the molecules may be neglected in comparison with the kinetic energy of the free molecule, and in which the volume of the molecular mass may be neglected in comparison with the whole volume of the gas — *i. e.*, a gas in which the Boyle-Gay-Lussac-Avogadro Law maintains, the volume may be considered as a simple function of the temperature and pressure; so we may write the relation:

$$dv = \left(\frac{\partial v}{\partial p}\right)_\theta dp + \left(\frac{\partial v}{\partial \theta}\right)_p d\theta, \tag{1}$$

where $v$, $p$, and $\theta$ are the volume, pressure, and absolute temperature respectively, and the subscripts indicate the variables that have been regarded as constant during the respective variations. We may also write the fundamental relation:

$$dp = \left(\frac{\partial p}{\partial v}\right)_\theta dv + \left(\frac{\partial p}{\partial \theta}\right)_v d\theta, \tag{2}$$

in which the symbols have the same meaning as in equation (1). Either one of these fundamental equations is sufficient to determine the thermodynamic conditions of an ideal gas.

For an ideal gas we have also the characteristic equation:

$$pv = R\theta. \tag{3}$$

It may be shown[1] that if $C_v$ and $C_p$ are the specific heats, respectively,

---

[1] Planck, Thermodynamics, p. 56.

$$C_v = \left(\frac{\partial u}{\partial \theta}\right)_v, \tag{4}$$

and

$$C_p = \left\{\left(\frac{\partial u}{\partial v}\right)_p + p\right\}\left(\frac{\partial v}{\partial \theta}\right)_p. \tag{5}$$

Since the velocity of sound through a gas depends on the ratio of its specific heats, this ratio may be conveniently determined by measuring the velocity of sound.

For the velocity of sound, we have the equation,

$$u^2 = -\gamma v^2\left(\frac{\partial p}{\partial v}\right)_\theta. \tag{6}$$

where $u$ is the velocity of sound and $\gamma$ the ratio of the specific heats.

Equation (6) may be written

$$u^2 = \gamma p v\left\{1 - \frac{1}{p}\left(\frac{\partial(pv)}{\partial v}\right)_\theta\right\}. \tag{7}$$

Hence we may write

$$\gamma = \gamma'\rho\left(\frac{\lambda}{\lambda'}\right)^2\left\{1 - \frac{1}{p}\left(\frac{\partial(pv)}{\partial v}\right)\right\}, \tag{8}$$

where $\gamma$ and $\gamma'$, and $\lambda'$ and $\lambda'$ are the ratios of the specific heats, and the wave-lengths of sound, respectively.

The ratio of the specific heats for any gas is determined by the ratio of the internal, or atomic, energy of the molecule to the transitional energy of the molecule. If, then, a certain quantity of energy $U$ be given to a molecule by the application of heat, and if $U_1$ is the part of $U$ taken up by the atoms of the molecule, and $U_2$ the part taken by the molecule to increase its kinectic energy of translation, and if $\beta$ is the ratio of the atomic to the molecular energies: then

$$\beta = \frac{U_1}{U_2} \tag{9}$$

and for a perfect gas we have the relation,

$$\beta + 1 = \frac{2}{3(\gamma - 1)}. \tag{10}$$

Equation (10) maintains for an ideal gas in which equation (3) is the characteristic equation. For a vapor or gas which does not follow the Boyle-Gay-Lussac-Avogadro law, we may write for the characteristic equation

$$pv = R\theta + \varphi(p, v, \theta).$$

From equations (3), (4), (5), (10) and (11), we may easily deduce the functional equation:

$$\begin{aligned}\gamma - 1 = \frac{2}{3(\beta + 1)}\Bigg\{ 1 &+ \frac{1}{v}\frac{\partial\varphi}{\partial p} + \frac{1}{p}\frac{\partial p}{\partial v} + \frac{2}{R}\frac{\partial\varphi}{\partial\theta} + \cdots \\ &- \frac{\varphi}{pv} - \frac{\varphi}{pv^2}\frac{\partial\varphi}{\partial p} - \frac{\varphi}{p^2v}\frac{\partial\varphi}{\partial v} - \frac{2\varphi}{Rpv}\frac{\partial\varphi}{\partial\theta}\cdots\Bigg\}.\end{aligned} \tag{12}$$

Writing the characteristic equation of Clausius in the functional form:

$$R\theta = p(v - a) + \frac{K}{\theta(v + b)^2}, \tag{13}$$

and making the assumption that $a$ and $b$, for air at normal temperature and pressure, are small in comparison with $v$; and neglecting quantities of the second order, we find,

$$\beta + 1 = \frac{2}{3}\frac{1}{(\gamma - 1)}\left\{ 1 + \frac{4}{p}\frac{\partial(pv)}{\partial v} \right\}, \tag{14}$$

writing Van der Waals's equation in the functional form

$$pv = R\theta + \left(\frac{ab}{v^2} + pb - \frac{a}{v}\right), \tag{15}$$

and making similar assumptions we have,

$$\beta + 1 = \frac{2}{3}\frac{1}{\gamma - 1}\left\{ 1 + \frac{2}{p}\frac{\partial(pv)}{\partial v} \right\}, \tag{16}$$

## Apparatus for Determining the Velocity of Sound.

The apparatus for determining the velocity of sound in gases or vapors at low temperature was the usual form of the double Kundt sound apparatus. A glass vibrating rod, one meter in length and 1.14 cm. in diameter was clamped for its first overtone. Sound tubes, of similar dimensions, were fitted to each node, by suitable stoppers, with delivery tubes for the introduction of dry air and the gases to be experimented with. One of these sound tubes was fitted in a long, cylindrical, unsilvered Dewar bulb made especially for these experiments. This bulb was 72 cm. long and 7.8 cm. external diameter ; and was fitted to the sound tube by two rubber stoppers, carefully ground in shape and forced in by wooden clamps, clamped together by tension screws. The delivery tubes, for the entrance of the liquid air and the escape of the vapor, passed through these stoppers. It was found necessary to have two stoppers, because the inner stopper, which was in contact with the liquid air, when the bulb was filled, became hard and contracted away from the Dewar bulb ; so that the Dewar bulb could not be made to contain the liquid air. It was also found, that if the stoppers were cut so that when they were forced over the sound tube they were under tension transversely, the extra tension due to the contraction at liquid air temperature caused the stoppers to split longitudinally at the point where they were pierced by the delivery tubes. In order to avoid this, the stoppers were cut in such a manner that when clamped in position by the screw clamps, they were under compression. With this arrangement it was found possible to fill the Dewar bulb with liquid air and maintain the temperature quite constant for an hour or more.

In order to measure the temperature at which the velocity of sound was determined, a resistance thermometer was introduced into the sound tube. This was supported by a wire frame which fitted into the tube. The wires for the thermometer and the leads were led through the stopper, which closed one end of the sound tube ; the other end being sealed. The device used to adjust the length of the air column in the sound tube consisted of a cork fitted to the end of a long glass rod (which was also passed through the stopper). In order to separate this part of the apparatus completely from the standard sound tube, in which air was always the medium, a stopper was fitted inside the vibrating tube *A*, at one of its nodes. Corks were also fitted to the ends of the vibrating tube by means of fish glue. The fish glue was found to stand the temperature of liquid air better than other forms of glue, although even it became quite hard and brittle at low temperature. The standard tube was fitted with a cork, which could be adjusted by means of a glass tube, passing through the stopper at the farther end of the tube. This part of the apparatus is shown in diagrammatic form in Fig. 1.

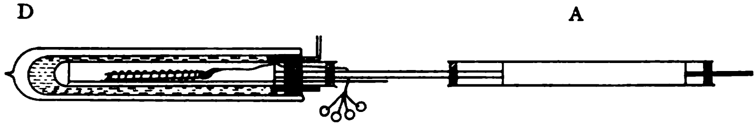

Fig. 1.

The pressure in the sound tube could be measured by an open mercury manometer.

*To Fill the Dewar Bulb.* — When the apparatus was all in place, it was necessary to fill the Dewar bulb with liquid air, while it remained in a horizontal position, in order that the cork filings, used to mark the position of the nodes, should not be disturbed. In order to lead in the liquid air against the pressure of the air evaporating in the large Dewar bulb, a third cylindrical Dewar bulb, unsilvered, was fitted with three tubes entering a rubber stopper, clamped into place by clamps similar to those on the Dewar bulb *D*. One of these tubes reached nearly to the bottom, the other two passing only through the stopper. The first of these tubes was connected to the delivery tube leading into the Dewar bulb *D*. One of those, that passed only through the stopper, was connected to the compression siphon, which in turn was fitted to the spherical retaining Dewar bulbs; the other was left open to the air. When this small cylindrical bulb had been filled with the liquid air, the rubber tube connecting it to the spherical Dewar bulb was closed by a pinch cock, the one that had been open to the air was also closed, and the liquid air was forced from this bulb into the horizontal cylindrical bulb *D*, by the pressure produced by the vaporization of the air in the small cylindrical Dewar bulb. The apparatus and connections are shown in Fig. 2.

*Measurements of Temperature.* — The temperature of the standard sound tube was determined by two mercury thermometers reading to tenths of a degree centigrade, suspended with their bulbs in contact with the outer surface of the glass tube.

The temperature in the comparison sound tube was measured by a resistance thermometer, mounted as near as possible to the center of the portion of the tube in which the sound waves were produced. A copper thermometer, instead of the usual platinum thermometer, was used. The copper thermometer had the advantage of having no junctions of dissimilar metals at points of varying temperature, which condition could not have been avoided in a platinum thermometer, except by leading the platinum wires outside the Dewar bulb.

*The Copper Thermometer.*—The copper thermometer was made by winding, noninductively, about eight meters of double silk insulated copper wire, diameter .018 cm., on a small glass tube 17.7 cm. in length. The ends of these wires were led out through a glass tube which passed through the rubber stopper, closing the end of the sound tube. The leads were taken from the same spool of wire, and were led in through the same tube parallel to the thermometer wires, and passed through the glass tube around which the thermometer wire was wound. The four wires were led to binding posts, and a plug switch-key, which was connected by wire cables to the Wheatstone's bridge in another part of the room.

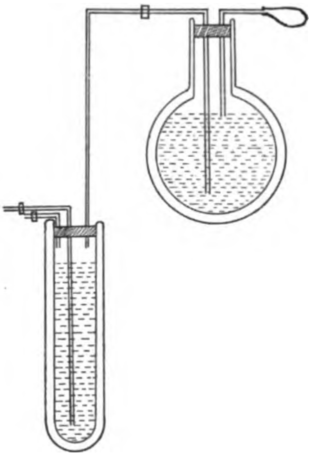

Fig. 2.

*Measurement of Wave-length.*—The half wave length, in the standard tube was measured by placing a meter measure directly beneath the sound tube. Those in the comparison tube were measured by a bifilar index, so arranged that the nodes could easily be read, even while the large Dewar bulb contained liquid air. The position of the bifilar index was determined by two meter measure, parallel to the comparison tube, along which the bifilar index was caused to slide.

*Calibration of Copper Thermometer*—The copper thermometer was calibrated by determining the resistance at three fixed points. The points selected were: the temperature of steam, over boiling water, at known pressure, the temperature of melting ice, and the temperature of liquid air of known vapor composition. Since the temperature of liquid air could only be determined by its analysis and the use of Baly's curve, a number of determinations were made at this temperature, with air having varying compositions, and the curve was smoothed through these points. Table I. gives the result of the calibration of the copper thermometer, from which the calibration curve, Fig. 3, is drawn, each measurement being the mean result of several readings.

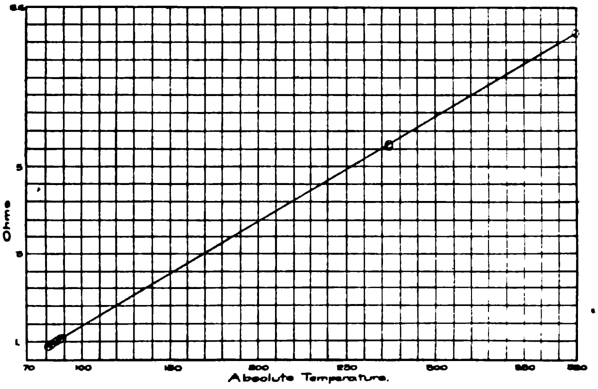

Fig. 3.

Table I.

| No. of Readings Taken. | Resistance in Ohms. | Temperature Absolute. | Constant Temperature Substance. |
|---|---|---|---|
| 10 | 8.019 | 372.9 | Steam. |
| 10 | 5.669 | 273.0 | Ice. |
| 10 | 5.664 | 273.0 | Ice. |
| 10 | 5.660 | 273.0 | Ice. |
| 10 | 3.698 | 193.0 | $Co_2$ + ether. |
| 10 | .957 | 82.1 | Liquid air. |
| 10 | .980 | 83.4 | " " |
| 8 | 1.007 | 84.8 | " " |
| 10 | 1.044 | 85.96 | " " |
| 10 | 1056 | 86.66 | " " |

*Method of Combining the Results of the Measurements of the Half Wave-Lengths.* — In the standard sound tube, where the adjustment of the distance between the end of the vibrating rod and adjustable cork could be obtained with very close approximation, before the experiment began, and in which the cork dust could be redistributed by rotating the tube; well defined and perfectly uniform nodes could always be obtained. The positions of the nodes in either tube were measured successively to the nearest millimeter, and the readings were combined to obtain the mean value of a half wave-length.

Several methods of combining a series of measurements, in order to give a mean result, suggest themselves. If $n$ be the number of nodes measured, and $r$ be the number of any reading, (1) we may form the differences $r - (r + 1)$ etc. to the difference $(r - n)$ giving $n - 1$ differences, and take the mean of these differences; (2) we may form the differences $r - (n/2 + r)$, etc. to the difference $(r - n)$ and take the sum of these differences divided by $(n/2)^2$ if $n$ is even, and by $(n/2 + 1/2)(n/2 - 1/2)$, if $n$ is odd; (3) we may form the differences $r - n$, $r - ](n - (r - 1)]$ etc., and divide the sum of these differences by $(n/2)^2$, if $n$ is even and by $(n/2 + 1/2)(n/2 - 1/2)$ if $n$ is odd. The first of these methods uses each half wave-length but once, and any errors in the measurements of the position of the nodes enter directly into the half wave-lengths. The second and third methods use respectively, the same number of half wave-lengths, *i. e.* $(n/2)^2$, if $n$ is even, and $(n/2 + 1/2)(n/2 - 1/2)$, if $n$ is odd. The only difference in the second and third methods being a difference in the distribution of the errors in the readings.

In measuring a series of half wave lengths, if the nodes are not all equally distinct, the readings of the individual nodes may be given weights; the resulting differences, between weighted nodes, will then carry with them the weights of the nodes. In measuring the half wave-lengths, in the comparison sound tube in the Dewar bulb, I found it convenient to use a combination of the second and third methods, using the third method without regard to the weights given each node, and using the second method to combine these nodes that had the highest weights assigned to them. The combination of these two methods gave very consistent results.

## DETERMINATION OF THE VELOCITY OF SOUND IN AIR.

My first idea was to determine the velocity of sound in air, oxygen, nitrogen, and possibly hydrogen, at the temperature of liquid air only, and at atmospheric pressure. The first determinations made in air, and oxygen, had this object in view.

Each determination was made in the following manner: When all parts of the apparatus were in place, and the cork dust uniformly distributed over the interior of the sound tubes, the sound tubes were filled with dry, carbon dioxide free air.

The Dewar bulb was then filled with liquid air as already described. As the air in the sound tube cooled, causing the pressure, as indicated by the manometer, to decrease, more air was allowed to flow into the sound tube. For the first determinations in air, the sound tubes were at atmospheric pressure. One observer followed the resistance of the thermometer, by means of the Wheatstone bridge and galvanometer; while the other observer manipulated the apparatus for filling the Dewar bulb, and at the proper time produced the sound wave. When the Dewar bulb was filled with liquid air, and the resistance thermometer indicated that the column of air in the sound tube had reached a steady temperature; the vibrating rod was bowed by rubbing it with a damp cloth. The length of the column of air between the two corks was adjusted, until good nodes were obtained in both sound tubes, the temperature, as indicated by the resistance thermometer, and by the mercury thermometer, near the standard tube, were noted; and the nodes were measured. I could usually obtain one series of measurements of the nodes in the comparison sound tube in the Dewar

### TABLE II.

*Velocity of Sound in Air at the Temperature of Liquid Air.*

| No. of Experiment. | $R$ Resistance in Ohms. | $\theta$ Tempt. Absolute. | $\theta'$ Tempt. Absolute. | $P$ cm. of Mercury. | ⅓ $\lambda$ cm. | ½ $\lambda'$ cm. | $u'$ cm./sec. | $u$ cm./sec. | $u''$ cm./sec. |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 1.810 | 117.5 | 295.1 | — | 1.9856 | 3.289 | 34,559 | 20,863 | 21,800 |
| 2 | 1.255 | 94.8 | 295.0 | 74.38 | 1.7744 | 3.2775 | 34,553 | 18,705 | 19,580 |
| 3 | 1.194 | 92.5 | 297.0 | 74.50 | 1.7362 | 3.2910 | 34,673 | 18,296 | 19,350 |
| 4 | 1.152 | 90.7 | 293.8 | 74.36 | 1.7261 | 3.2791 | 34,483 | 18,152 | 19,170 |
| 5 | 1.218 | 93.5 | 294.3 | 73.47 | 1.7305 | 3.2850 | 34,511 | 18,180 | 19,450 |
| 6 | 1.200 | 91.5 | 298.0 | 73.22 | 1.7306 | 5.304 | 34,733 | 18,193 | 19,250 |
| 7 | 1.185 | 92.0 | 292.4 | — | 1.738 | 5.233 | 34,400 | 18,493 | 19,380 |

bulb before the liquid evaporated. Other measurements were made at room temperature, and corrected for the expansion of the glass tube.

Table II. sets forth the results of seven measurements of the velocity of sound in air.

In Table II. the absolute temperature is denoted by $\theta$, the wave length by $\lambda$, and the velocity of sound by $u$. The primes refer in each case to the temperature, wave lengths, and velocity, in the standard tube, while $u''$, in the last column, is the velocity calculated from the formula for the velocity of sound, assuming the Boyle-Gay-Lussac-Avogadro law to hold down to liquid air temperature. For the velocity of sound in dry air at 0° I have taken, in accordance with the International Congress of Physics, Paris, 1900, the value 33136 cm. per sec. $u''$ has been calculated from the formula

$$u = u_0 \sqrt{1 + at}.$$

$\lambda$ and $\lambda'$ are mean values of several measurements of the wave length, measured at the temperature $\theta$ and $\theta'$ respectively. The velocity $u$ at the temperature $\theta$ was calculated from the relation.

$$u = u' \frac{\lambda}{\lambda'}.$$

The absolute temperature $\theta$ was taken from the calibration survey of the copper thermometer, while $\theta'$ was found by assuming the absolute temperature to have the value $-273°$.

### MEASUREMENT OF THE VELOCITY OF SOUND IN OXYGEN.

The method for measuring the velocity of sound in oxygen was similar to that for the measurement of the velocity of sound in air. The oxygen used, having been obtained by the electrolysis of water, contained traces of hydrogen. In order to remove the hydrogen, the oxygen was liquefied in a bulb immersed in liquid air. The tube was then exhausted and the vapor from the liquid oxygen allowed to pass into it.

Under atmospheric pressure, the oxygen again liquefied in the sound tube. At somewhat reduced pressure, however, the oxygen could be maintained in its vapor form even at the temperature of liquid air. The sound wave was passed through this saturated vapor of oxygen, and, when the adjustment had been secured, and good flutings obtained, the temperature and pressure were noted, as in the air determinations.

It was necessary to make the determination at less than atmospheric pressure. This required maintaining a partial vacuum in the sound tube at the temperature of liquid air. Several determinations were made ; but, as a very slight variation in the temperature produced a marked change in the pressure at which the oxygen would remain in the vapor condition, the determinations were not all made at the same pressure. This introduced into the results two variables, pressure and temperature. The number of the results, at varying pressure, has not been sufficient to establish any real dependence upon pressure ; but the irregularity of the results showed some variable factors other than temperature. The difficulty of maintaining even a partial vacuum, at this low temperature, may account for some of the results that are higher than might have been expected from the results with air. An error due to either of these possible variations would have resulted in the increase of the wave-length of sound in the oxygen.

Table III. exhibits the results of the determination of the velocity of sound in oxygen at the temperature of liquid air. The symbols are used in a similar manner as in Table II.

Table III.

*Velocity of Sound in Oxygen at Temperature of Liquid Air.*

| No. of Experiments. | $R$ Resist. in Ohms. | $\theta$ Degrees Absolete. | $\theta'$ Degrees Absolute. | $P$ Pressure in cm. of Mercury. | $\frac{1}{2}\lambda$ Wave-Length in cm. | $\frac{1}{2}\lambda'$ Wave-Length in cm. | $u$ Velocity in cm./sec. | $u'$ Velocity in cm./sec. | $u''$ Theoretical Velocity in cm./sec. |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 1.227 | 94.0 | 295.1 | 60.5 | 1.6276 | 3.274 | 17,177 | 34,550 | 18,550 |
| 2 | 1.574 | 107.7 | 291.2 | 50.8 | 1.8009 | 3.267 | 18,913 | 34,310 | 19,860 |
| 3 | 1.094 | 88.4 | 292.8 | 48.35 | 1.6489 | 3.266 | 17,368 | 34,400 | 18,000 |
| 4 | 1.532 | 106.1 | 293.1 | 40.15 | 1.7546 | 3.271 | 18,468 | 34,430 | 19,710 |
| 5 | 1.100 | 89.0 | 291.8 | 34.9 | 1.684 | 3.2697 | 17,692 | 34,350 | 18,040 |
| 6 | 1.117 | 89.7 | 290.5 | 34.0 | 1.695 | 3.2785 | 17,724 | 34,280 | 18,110 |
| 7 | 1.127 | 90.0 | 291.5 | 49.94 | 1.6393 | 3.2357 | 17,392 | 34,320 | 18,130 |

## Ratio of the Specific Heats.

To determine the ratio of the specific heats, at the temperature of liquid air, we have to solve equation 8, placing for an ideal gas

$d(pv) = 0$, and for a gas which does not follow the laws of an ideal gas we must solve equation 8, giving its values for Clausius's or Van der Waals's characteristic equation.

In order to solve these equations, it became necessary to determine the density of the air, or gas, at the temperature at which the wave-length $\lambda$ had been determined, relative to the density at the temperature at which $\lambda'$ had been measured.

From the ratio of the specific heats $\gamma$ it was possible also to find the value of the ratio of the internal to the translational energy of the molecule, from formula 14 or 16. This involved the determination of the variation of the density with pressure; that is, the evaluation of the differential coefficient at the temperature $\theta$.

## Determination of the Density of Air at the Temperature of Liquid Air.

*Apparatus.* — An air thermometer bulb of about thirty cubic centimeters capacity was connected by a capillary glass tube to a volumetric burette of 100 c.c. capacity, graduated to fifths of a c.c. The burette was attached to a levelling tube, by a meter or more of heavy rubber tubing; and the apparatus was partly filled with mercury. The apparatus is shown in Fig. 4. The graduated burette, $A$, was connected to the gas cylinder, through $f$, and to the air pump and manometer through $g$. $C$ was connected to the levelling tube, $B$, by rubber tubing, with a pinch-cock at $n$. By lowering the levelling tube the mercury could be run out into $B$; the pinch-cock at $n$ closed; then by closing the delivery tube, $f$, the apparatus could be exhausted through $g$ and filled with the gas whose density was to be found by opening the delivery tube, $f$.

*The Air Thermometer Bulb.* — The air thermometer bulb, $D$, shown enlarged in Fig. 4 at $D'$, was made by drawing down a piece of cylindrical glass tubing, and sealing to it the capillary tube $l$. The platinum thermometer was then sealed in, and the tube was sealed off, just below the end of the platinum thermometer.

*The Platinum Resistance Thermometer.* — The platinum thermometer was made of fine platinum wire, laced through holes drilled in a strip of mica, $M$. This fine platinum wire was soldered to heavier platinum leads, $a$ and $b$, which supported the thermometer, and which were led out, through the walls of the air thermometer, to the copper leads above. The dummy, *d*, a piece of platinum wire of the same diameter as the heavy platinum wire, was soldered to the two copper leads, at the same position with respect to the thermometer bulb as were the thermometer leads. The copper leads were led to binding posts in a hard rubber base. This rubber base was divided into halves and supported by clamping tightly to the capillary tube, *l*. The binding posts were then connected, by twin cables, to the same switch key as was used for the copper thermometer; this, in turn, being connected by cable to the bridge.

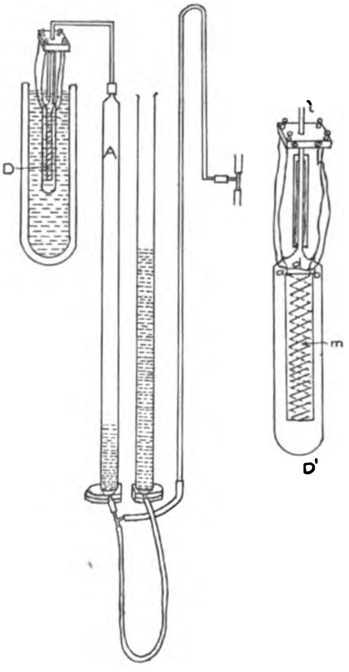

Fig. 4.

I made several of these air thermometer bulbs, and platinum thermometers, before one was obtained that gave consistent results. The chief difficulty was encountered in constructing a bulb that would stand liquid air temperature at the point where the heavy capillary tube began. This difficulty was obviated by covering some eight centimeters of the capillary with tinfoil. A piece of rubber tubing was fitted over this, to keep it in place, and to avoid any possibility of short circuiting the galvanometer by the platinum leads coming in contact with the tinfoil. The tinfoil acted as an equalizer of the temperature over the surface of the heavy capillary tube, and prevented all further breaks at this point. These facts are mentioned, mainly, to explain the cause for the use of several different air thermometer bulbs, during the determination of density. The different bulbs will be referred to by number.

## DETERMINATION OF THE VOLUME OF THE AIR THERMOMETER BULB.

The volume of the bulb, fitted with the platinum thermometer, was determined by weighing it, filled with distilled water. The volume of the capillary tube was determined by means of a thread of mercury.

The data for determining the volume of the different bulbs, used in my determination of the density of air, and other gases, are exhibited in Table IV.

### TABLE IV.

*Volume of Bulbs.*

| 1<br>No. | 2<br>$W$<br>grams. | 3<br>$W'$<br>grams. | 4<br>T° C. | 5<br>Temp. of Water °C. | 6<br>$V$<br>grams. | 7<br>$V$<br>cc. | 8<br>$V$<br>cc. | 9<br>$V$<br>cc. |
|---|---|---|---|---|---|---|---|---|
| 1 | 149.703 | 245.832 | 21.4 | 21.5 | 96.129 | 96.490 | 96.186 | 95.626 |
| 2 | 125.051 | 170.652 | 18.8 | 17.5 | 45.6007 | 45.7154 | 45.42 | 45.20 |
| 3 | 129.085 | 159.4798 | 18.6 | 17.6 | 30.3948 | 30.472 | 30.172 | 30.018 |
| 2 A | 128.106 | 164.356 | 22.1 | 22.1 | 36.250 | 36.370 | 36.070 | 35.900 |
| 5 | 132.922 | 162.344 | 16.5 | 18.5 | 29.422 | 29.517 | 29.207 | 29.057 |

Column 1 gives the number by which the bulb was known in the experiment; column 2 gives the weight of the bulb, when filled with dry air; column 3, the weight of the bulb, when filled with water; column 4 and 5 give the temperature at which the respective weighings were made; column 6, the apparent volume of the bulb and capillary tube, obtained by subtracting $W$ from $W'$; column 7, the volume at 20° C.; column 8 gives the volume of the thermometer bulb less the volume of thc capillary tube which was not at the liquid air temperature, and column 9, the volume of the thermometer bulb at $-190°$ C.

## CALIBRATION OF PLATINUM THERMOMETERS IN THE AIR THERMOMETER BULBS.

The platinum thermometers were calibrated, after they were sealed into the bulbs, by determining the resistance at the three points, *i. e.*, steam over boiling water, melting ice, and liquid air.

Table V gives the calibration of the thermometers. The calibration curve for one of the thermometers is exhibited in Fig. 5.

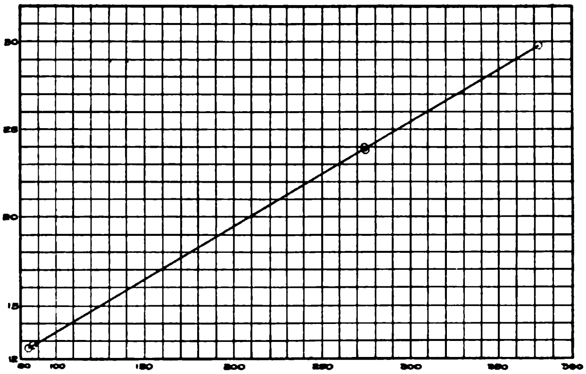

Fig. 5.

### Table V.

*Calibration of Thermometers in Air — Thermometer Bulbs.*

| Number. | Substance Used to Determine Fixed Point. | No. of Readings Taken. | Resistance of Therm. in Ohms. | Tempt. Absolute. |
|---|---|---|---|---|
| 1. | Steam. | 10 | 3.090 | 372.22 |
| | | 10 | 3.000 | 372.24 |
| | Ice. | 10 | 2.219 | 273.00 |
| | | 10 | 2.224 | 273.00 |
| | Liquid air. | 10 | 0.674 | 84.3 |
| | | 10 | 0.684 | 87.0 |
| | | 10 | 0.682 | 85.75 |
| 2. | Steam. | 10 | 7.484 | 372.48 |
| | Ice. | 10 | 5.546 | 273.00 |
| | Liquid air. | 10 | 1.998 | 86.5 |
| 3. | Steam. | 10 | 4.146 | |
| | Ice. | 10 | 3.117 | 273.00 |
| | Liquid air. | 10 | 1.278 | 88.9 |
| 5. | Steam. | 10 | 29.57 | 372.1 |
| | | 10 | 29.81 | 372.1 |
| | Ice. | 10 | 23.90 | 273.0 |
| | | 10 | 24.04 | 273.0 |
| | Liquid air. | | 12.716 | 83.84 |
| | | | 12.908 | 85.77 |

## DETERMINATION OF THE RELATIVE DENSITY OF AIR AT THE TEMPERATURE OF LIQUID AIR.

*Method.* — After the apparatus had been well washed with dry air, it was exhausted; and the air was led in through *f*, having first passed through a cooling coil, placed in liquid air, which removed all traces of moisture or carbon-dioxide from the air. When the apparatus was filled with this pure air, the pinch cock at *n* was opened; and the mercury, flowing into the burette *A*, entrapped a certain volume of air. The mercury in *A* and *B* was now brought to the same level, and the barometer, which gave the pressure of the air in the apparatus, was read. The temperature of the air in the thermometer bulb was determined by the platinum thermometer, that in the burette by a mercury thermometer, suspended near *A*. The volume was then read on the burette. This gave the total volume of the gas enclosed. The air thermometer bulb, *D*, was immersed in liquid air. After the gas in the air thermometer bulb had attained a stationary temperature, as shown by the constancy of the resistance of the platinum thermometer, the mercury in the levelling tube was again brought to the same level as the mercury in the burette, and the temperatures of the gas in the air thermometer bulb, and that remaining in the burette, were determined by their respective thermometers. The pressure was again determined by means of the barometer. This gave sufficient data for the determination of the density of the air at the temperature indicated by the platinum thermometer, relative to the density of the air at room temperature.

To determine the relative density at any other than atmospheric pressure, the leveling tube was raised or lowered by any amount whatever within the limits of the burette; and the pressure difference was measured by a meter measure, placed behind the burette and levelling tube. The position of the mercury, in both the levelling tube and the burette, was determined by aluminum indices, made to slide over the glass tubes. These indices carried verniers, so that the scale on the meter measure could be read to tenths of millimeters. For low pressures the burette and bulb were filled, when at room temperature, at a pressure less than one atmosphere.

The burette was graduated to 0.2 cc., and could be estimated to 0.02 cc. This gave an accuracy of two parts in a thousand, in the measurement of volume. The pressure could be measured to one part in a thousand. The temperature of gas in the burette could be read to tenths of a degree; and in the bulb, to the tenth of a degree from the calibration curve, which made the least reading for temperatures about one part in two thousand. The following tables exhibit the determinations of the relative densities of air, at various temperatures and pressures. Table VI. exhibits the den-

### Table VI.

*Relative Density of Air, at Various Temperatures, Pressure Constant. Bulb No.* 5, *Pressure* 73.49 = $p$.

| No. of Determination. | Bulb No. | Temperature. | | Density. $\rho$ |
|---|---|---|---|---|
| | | $t^\circ$ C. | $\theta^\circ$ Absolute. | |
| 1 | 1 | 20.6 | 83.8 | 3.661 |
| 2 | 3 | 17.8 | 82.5 | 3.656 |
| 3 | 3 | 17.9 | 83.5 | 3.656 |
| 4 | 3 | 17.9 | 83.5 | 3.655 |
| 5 | 3 | 17.9 | 83.5 | 3.655 |
| 6 | 2A | 21.0 | 82.5 | 3.647 |
| 14 | 5 | 17.2 | 83.6 | 3.595 |
| 20 | 5 | 17.4 | 83.5 | 3.578 |
| 25 | 5 | 17.4 | 84.6 | 3.584 |

### Table VII.

| No. of Determination. | Temperature at Which Determinations were Made. | | Density. $\rho$ |
|---|---|---|---|
| | $t$ | $\theta$ | |
| 1 | 16.9 | 290.5 | 1.000 |
| 2 | 16.9 | 255.5 | 1.1432 |
| 3 | 16.9 | 238.5 | 1.2297 |
| 4 | 16.9 | 237.0 | 1.2382 |
| 5 | 16.9 | 235.2 | 1.2450 |
| 6 | 16.95 | 219.5 | 1.3490 |
| 7 | 17.00 | 197.0 | 1.5197 |
| 8 | 17.00 | 178.4 | 1.7312 |
| 9 | 17.00 | 290.0 | 1.000 |
| 10 | 17.00 | 221.0 | 1.3439 |
| 11 | 17.00 | 175.6 | 1.7478 |
| 12 | 17.00 | 147.6 | 2.1516 |
| 13 | 17.10 | 114.4 | 2.6699 |
| 20 | 17.40 | 83.5 | 3.5778 |

sity, at the temperature of liquid air and atmospheric pressure, relative to the density at room temperature at atmospheric pressure. Table VII. exhibits the density with varying temperature, pressure constant, and Table VIII. exhibits the same with varying pressure, temperature constant.

TABLE VIII.

*Relative Density of Air at Various Pressures, Temperature Constant.*

| Number. | Tempt. at which Determinations were Made. | | Pressure p. in cm. of Mercury. | Density. $\rho$ |
|---|---|---|---|---|
| | $t$. | $\theta$ | | |
| 14 | 17.20 | 83.6 | 69.59 | 3.5950 |
| 15 | 17.40 | 83.5 | 61.09 | 3.5836 |
| 16 | 17.35 | 83.5 | 55.17 | 3.5768 |
| 17 | 17.35 | 83.5 | 50.95 | 3.5758 |
| 18 | 17.35 | 83.5 | 43.97 | 3.5512 |
| 19 | 17.40 | 83.5 | 39.84 | 3.5464 |
| 20 | 17.40 | 83.5 | 73.49 | 3.5778 |
| 25 | 17.40 | 84.6 | 73.49 | 3.5836 |
| 26 | 17.40 | 84.6 | 84.49 | 3.5821 |

## DETERMINATION OF THE DENSITY OF OXYGEN.

The apparatus was the same as that for the density of air, and the method was identical. Oxygen liquefied at atmospheric pressure and liquid-air temperature. The point of liquefaction was determined by making a series of measurements at reduced pressures. As the pressure increased, the relative densities increased slightlyup to a certain point at which they increased much more rapidly and also became a function of the time that the bulb was kept at this low temperature. By plotting the relative densities as ordinates and the pressures as abscissa the graph made a sharp bend at the point of liquefaction.

The following tables give the relative densities of oxygen, as compared with oxygen at room temperature and atmospheric pressure. Table IX. gives the relative densities at varying pressure and constant or nearly constant temperature.

## DETERMINATION OF THE RATIO OF THE SPECIFIC HEATS.

Having determined the density of air and oxygen, at the temperature of liquid air, it was only necessary to compute from these data

### TABLE IX.

*Density of Oxygen, Temperature Constant, under Varying Pressure.*

| Number of Determination. | Temperature at which Determinations were Made. | | Pressure in cm. of Mercury $p$. | Density. $\rho$ |
|---|---|---|---|---|
| | $t$ | $\theta$ | | |
| 1 | 17.2 | 89.5 | 51.64 | 3.553 |
| 2 | 17.2 | 89.5 | 51.60 | 3.558 |
| 3 | 17.2 | 89.5 | 56.75 | 3.568 |
| 4 | 17.2 | 89.5 | 51.69 | 3.542 |
| 5 | 17.2 | 89.5 | 55.69 | 3.545 |
| 6 | 17.2 | 89.5 | 55.09 | 3.553 |
| 7 | 18.0 | 84.1 | 55.90 | 3.524 |
| 8 | 18.0 | 84.1 | 51.90 | 3.515 |
| 9 | 18.0 | 84.0 | 49.00 | 3.512 |
| 10 | 18.0 | 84.0 | 45.40 | 3.547 |
| 11 | 18.0 | 84.0 | 42.91 | 3.533 |
| 12 | 18.0 | 84.0 | 40.82 | 3.530 |
| 13 | 18.0 | 84.0 | 38.13 | 3.538 |
| 14 | 18.0 | 84.0 | 36.14 | 3.584 |
| 15 | 18.0 | 84.0 | 34.34 | 3.562 |

the density of air and oxygen, at the temperature at which the determination for the velocity of sound was made, relative to the density of air in the standard tube, in order to give sufficient data for the determination of the specific heats, at the temperature at which the velocity of sound was measured, from the formula,

$$v = v'\rho\left(\frac{\lambda}{\lambda'}\right)^2$$

### TABLE X.

*The Ratio of the Specific Heats in Air.*

| No. | $P$ | $\theta$ | $\theta'$ | $\rho$ | $\lambda$ | $\lambda'$ | $\gamma$ |
|---|---|---|---|---|---|---|---|
| 1 | | 117.5 | 295.1 | 2.69 | 1.9856 | 3.2890 | 1.386 |
| 2 | 74.38 | 94.8 | 295.0 | 3.32 | 1.7744 | 3.2775 | 1.370 |
| 3 | 74.50 | 92.5 | 297.0 | 3.41 | 1.7362 | 3.2910 | 1.337 |
| 4 | 74.36 | 90.7 | 293.8 | 3.44 | 1.7261 | 3.2791 | 1.342 |
| 5 | 73.47 | 93.5 | 294.3 | 3.33 | 1.7305 | 3.2850 | 1.300 |
| 6 | 73.22 | 91.5 | 298.0 | 3.45 | 1.7306 | 3.3040 | 1.333 |
| 7 | | 92.0 | 292.4 | 3.38 | 1.7380 | 3.2330 | 1.375 |

Table X. exhibits the results of the determination of the density, $P$, and the ratio of the specific heats $\gamma$. The value 1.408 was taken as the ratio of the specific heat for air at normal temperature and pressure. The first column refers to the number of the experiment. The column $P$ exhibits the pressure; $\theta$ and $\theta'$, the absolute temperature; $\lambda$ and $\lambda'$, the half wave-lengths; and $\gamma$ the ratio of the specific heats.

## DETERMINATION OF THE RATIO OF THE INTERNAL TO THE EXTERNAL ENERGY OF THE MOLECULES.

Having determined the ratio of the specific heats, the ratio of the internal to the external energy of the molecule, is found from equations 10, 14 or 16, depending on whether we use the simple relation, in which $pv = R\theta$, the characteristic equation of Clausius, or that of Van der Waals.

In order to evaluate either equation 14 or 16, we must determine the value of the expression $1/p[\partial(pv)/\partial v]_\theta$.

To find the variation of $pv$ relative to $v$, we measure the densities at different pressures. These measurements for air are exhibited in Table VIII.

Having assumed some arbitrary unit of pressure $pv$ is found by multiplying the reciprocal of $\rho$ by this pressure. The volume $V$, is computed by dividing the quantity $pv$ by the actual pressure, $P$. The values of $pv$ are plotted as ordinates, and the values of $V$, as abscissæ. The slope of the curve with the horizontal gives the value, $\partial(pv)/\partial v$; this, divided by the pressure at which the determination was made, gives the value of $1/p[(\partial pv)/\partial v]$

Table XI. gives the values of $\beta$ for air.

TABLE XI.

*Value of the Ratio of the Internal to the External Energy.*

| No. | $\gamma$ | $\frac{1}{p}\frac{d(pv)}{dv}$ | $\beta_1$ | $\beta_2$ | $\beta_3$ |
|---|---|---|---|---|---|
| 0 | 1.408 | .0000 | .614 | .634 | .634 |
| 1 | 1.385 | .0012 | .727 | .732 | .7295 |
| 2 | 1.370 | .0012 | .802 | .807 | .8045 |
| 3 | 1.337 | .0012 | .978 | .983 | .9805 |
| 4 | 1.342 | .0012 | .949 | .954 | .9515 |
| 5 | 1.300 | .0012 | 1.222 | 1.227 | 1.2245 |
| 6 | 1.333 | .0012 | 1.002 | 1.007 | 1.0045 |
| 7 | 1.375 | .0012 | .951 | .956 | .9535 |

Column $\beta_1$ is the value of the ratio of the internal to the external energy, deduced from the simple relation between $\gamma$ and $\beta$ given in equation 10; column $\beta_2$ is its value in accordance with Clausius' characteristic equation according to equation 14; and column $\beta_3$, its value according to Van der Waals' characteristic equation, from equation 16. Number 0 gives the value of $\beta$ at normal temperature and pressure.

## DETERMINATION OF THE VELOCITY OF SOUND AT TEMPERATURES BETWEEN THE TEMPERATURE OF THE ROOM AND THE TEMPERATURE OF LIQUID AIR.

Since the velocity of sound for both air and oxygen was found to be less than that calculated, on the assumption that the Boyle-Gay-Lussac-Avogadro law maintains down to the liquid air temperature, it was thought that it would be of interest to determine the velocity of sound at various temperatures up to the temperature of the room.

The apparatus, as set up for the measurement of the velocity of sound at liquid air temperature, was used for the determination at temperatures greater than that of liquid air. Liquid air was introduced into the Dewar bulb, as before, with the exception that, instead of completely filling the Dewar bulb only a small quantity of liquid air was introduced at a time. The sound tube in the Dewar bulb was then allowed to reach a minimum temperature, as indicated by the copper thermometer. It was found that at this point of minimum temperature the thermometer indicated that the temperature in the sound tube remained constant, or nearly constant, for three or four minutes; and a determination of the velocity of sound could easily be made in this time.

After making a determination in this manner more liquid air was introduced into the Dewar bulb; and a second determination was made at a lower temperature. From four to five determinations were made in this manner between room temperature and the temperature of liquid air. Two series of these determinations have been made in air and the results are exhibited in tables XII., and XIII.

After making the first series of measurements it occurred to me that, possibly, the temperature in the sound tube did not become uniform throughout the tube. In order to avoid any possible error from this source two metal strips were introduced into the sound tube, completely lining the sound tube, with a metallic lining, except a narrow strip, above and below, through which the position of the nodes could be determined. The second set of measurements was made with this temperature equalizer in the sound tube.

## TABLE XII.

*Velocity of Sound in Air at Various Temperatures. (Set 1.)*

| No. | $R$ | $\theta$ | $\frac{1}{2}\lambda'$ | $\frac{1}{2}\lambda$ | $V_\theta$ |
|---|---|---|---|---|---|
| 1 | 6.145 | 294.0 | 3.2187 | 3.2265 | 34,400 |
| 2 | 4.133 | 212.6 | 3.233 | 2.7145 | 28,886 |
| 3 | 3.236?<br>2.936 | 175.8<br>163.0 | 3.233 | 2.3450 | 24,951 |
| 4 | 2.634?<br>2.334 | 151.4<br>138.4 | 3.233 | 2.1545 | 22,935 |
| 5 | 2.266 | 136.5 | 3.233 | 2.1070 | 22,419 |
| 6 | 1.185 | 92.0 | 3.233 | 1.738 | 18,493 |

## TABLE XIII.

*Velocity of Sound in Air at Various Temperatures. (Set 2.)*

| No. | $R$ | $\theta$ | $\theta'$ | $\frac{1}{2}\lambda'$ | $\frac{1}{2}\lambda$ | $V_\theta$ |
|---|---|---|---|---|---|---|
| 1 | 6.170 | 295.5 | 289.0 | 3.199 | 3.2220 | 34,470 |
| 2 | 6.082 | 292.0 | 290.7 | 3.206 | 3.1695 | 33,830 |
| 3 | 4.912 | 244.2 | 291.3 | 3.222 | 2.9092 | 30,892 |
| 4 | 3.005 | 166.8 | 291.3 | 3.222 | 2.3887 | 25,375 |
| 5 | 4.201 | 216.0 | 291.3 | 3.222 | 2.7550 | 29,261 |
| 6 | 3.033 | 167.5 | 291.3 | 3.222 | 2.3945 | 25,433 |
| 7 | 1.940 | 123.0 | 291.3 | 3.222 | 2.0405 | 21,673 |

## TABLE XIV.

*Velocity of Sound in Oxygen at Various Temperatures.*

| No. | $R$ | $\theta$ | $P$ | $\frac{1}{2}\lambda'$ | $\frac{1}{2}\lambda$ | $V\theta$ |
|---|---|---|---|---|---|---|
| 1 | 6.130 | 293.0 | 73.44 | 3.2205 | 3.0830 | 32,855 |
| 2 | 4.910 | 244.6 | 73.44 | 3.2357 | 2.6618 | 28,240 |
| 3 | 3.982 | 206.5 | 73.44 | 3.2357 | 2.4906 | 26,426 |
| 4 | 2.899 | 162.0 | 73.44 | 3.2357 | 2.1983 | 23,322 |
| 5 | 2.613 | 150.3 | 73.44 | 3.2357 | 2.1149 | 22,444 |
| 6 | 2.246 | 135.5 | 55.34 | 3.2357 | 1.9805 | 21,012 |
| 7 | 1.127 | 90.0 | 49.94 | 3.2357 | 1.6393 | 17,392 |

Table XIV. exhibits a set of measurements of the velocity of sound in oxygen at various temperatures between room temperature and the temperature of liquid air.

The determination of the velocity of sound in air and oxygen, as exhibited in Tables II., III., XII., XIII., and XIV. are exhibited graphically in Fig. 6.

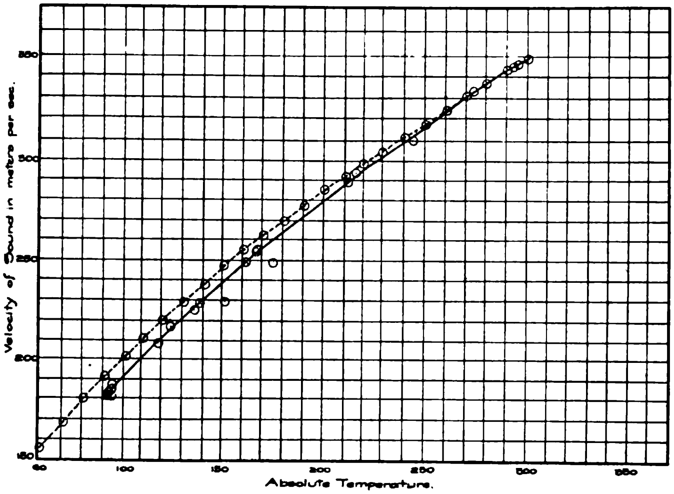

Fig. 6.

The velocity of sound is plotted as ordinates, and the absolute temperature as abscissæ. The curves are smoothed through the points. For comparison a curve (the broken line curve) which represents the velocity of sound, according to the formula,

$$u^2 = \gamma pv,$$

on the assumption that $\gamma$ is constant and $pv = R\theta$ is plotted along with the curve plotted from the experiments.

## Conclusion.

The results of the measurements of the velocity of sound show that the velocity of sound at low temperature does not follow the simple formula,

$$u^2 = \gamma pv.$$

If the pressure is constant, there remain two possible variables, $\gamma$ and $\rho$. From the determination of the density at temperature between 0° and — 190°, it appears that the density, $\rho$, increases, relatively, more than would be consistent with $pv = R\theta$; but that it does not quite compensate for the decrease in the velocity of sound, and, hence, we find that the ratio of the specific heats decreases, somewhat, at the lower temperatures. At these low temperatures the gas is in the vapor condition. From the variation in $\gamma$ it follows that there is a variation in the ratio of the internal to the external energy $\beta$.

The work detailed in this paper was undertaken during the summer of 1903. Through the courtesies of Professor Nichols and Dr. Shearer, the Physics Laboratory of Cornell University was placed at my disposal. The work was completed during the college year 1904 and 1905. I wish to take this opportunity of expressing my sincere thanks to professor Nichols and Dr. Shearer for many valuable suggestions during the progress of the work. I also wish to thank Dr. F. E. Kester for valuable assistance in making observations.

Physical Laboratory,
Cornell University, June, 1905.

# THE USE OF THE WEHNELT INTERRUPTER WITH THE RIGHI EXCITER FOR ELECTRIC WAVES.

BY A. D. COLE.

IN some earlier work with electric waves, generated by a Righi exciter and measured by a Klemenčič thermo-receiver,[1] it was found necessary to use a very sensitive galvanometer. Thus for most of the work a figure of merit of about $4.5 \times 10^{-9}$, in a 5-ohm galvanometer, was necessary.

Such sensitiveness in a galvanometer of resistance so low requires one to adjust its control magnet to produce a field so weak that the zero wanders badly and the vibration period is excessively long. This is a matter of serious consequence in these days when there is an electric railway or two in the near vicinity of nearly every physical laboratory. It is therefore desirable both for research and demonstration purposes to so increase the energy of the radiation as to allow the use of galvanometers of lower sensitiveness and shorter period.

As the integrated value of the energy is operative in receivers of the thermoelectric type, proportionately larger deflections are to be expected with an increase of frequency in the interrupter used with the induction coil. A test of this point was made several years ago by substituting a rotary break driven by an electric motor for the ordinary spring interrupter of the induction coil. Larger deflections were obtained in this way, but the action was quite irregular and the exciter soon became hot. So for the time the use of the ordinary interrupter was resumed.

Later, however, a plan for the constant circulation of oil through the exciter which had been adopted, gave promise of avoiding the troublesome heating effects of a high-frequency interrupter, and a new attempt was made. This time the Wehnelt interrupter was tried and was found to answer the purpose admirably. A 4.5-ohm. galvanometer whose figure of merit was $2.3 \times 10^{-9}$ gave deflections of about 800 mm. with the scale 1 meter distant. The control magnet was moved until the figure of merit was only $4 \times 10^{-8}$, and its double vibration period only 2.7 seconds. Now the sensitiveness was only about one-twentieth what it had been before and yet the deflections are sufficiently large. The zero was steady (even with cars running every minute on the neighboring electric line). Further the greatly diminished period made it possible to obtain series of readings in a fraction of the time necessary before.

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[1] Cole, A. D., Wied. Ann., 57, 298, 1896. PHYS. REV., 7, 225, 1898; 20, 268, 1905.

Considerable difficulty was found however at first in obtaining a form of interrupter which would remain in fairly constant condition for even an hour or two of steady use. The acid cell and the lead electrode were made of large size so that the interrupter would run cool, but the small electrode gave trouble. When made of platinum wire sealed into a glass tube it usually cracked out after a short time. The use of soft enamel glass for sealing in the wire reduced the difficulty, but did not remove it. An electrode which would not break was obtained by using several small platinum wires a millimeter or so apart sealed into the enameled tip. But these thin wires wore away too rapidly to be practical.

Various forms of adjustable electrode were tried. In these a single heavy platinum wire 1.4 mm. in diameter was used as an electrode. This was mounted in a surrounding glass tube of about 3.5 mm. internal diameter and projected through a plug or plate of insulating material at the lower end. Okonite insulation and rubber were first used for the plug, but they quickly softened by the heat and became disintegrated. Small discs cut from the bowl of a clay pipe were but little more durable. Compressed asbestos and a hard kind of talc were tried and rejected. Finally good results were obtained by using small discs cut out of a piece of close-grained slate. A small hole through the center of the disc allowed the platinum tip to be adjusted in length. This disc (see *a*, Fig. 1) was cemented to the end of the glass tube. The platinum wire was about 8 cm. long and soldered at *b* to one primary terminal of an induction coil. The cork shown at *c*, at the top of the glass tube, kept the tip from changing in length after it was suitably adjusted.

The tube usually projected down about 2 cm. into the weak acid of the cell. Details of construction are shown in the figure. The round battery jar of glass, 21 cm. high and 15 cm. in diameter, was filled to a depth of 13 cm with dilute sulphuric acid of specific gravity 1.05. One electrode was formed of a strip of lead 50 cm. long and 9 cm. wide, bent up into a U-shape so as to present about 720 sq. cm. of surface to the acid. The other electrode consisted of the 1.4 mm. platinum wire, projecting usually 4 mm. Acid so weak was chosen because the frequent removal and adjustment of the platinum tip was thus made more convenient and the small increase of resistance was unimportant since it was found best to use additional resistance in series with the cell for control.

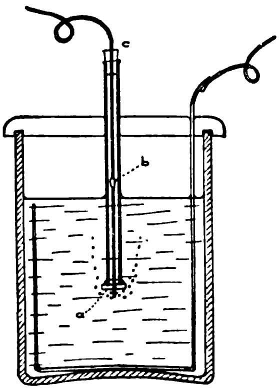

Fig. 1.

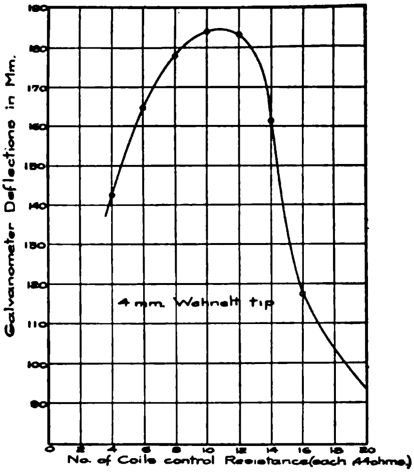

Fig. 2.

Alternating current of 110 volts was used for exciting this Wehnelt interrupter. When no resistance was used in series with it there was excessive heating, both of the interrupter and of the Righi exciter. This gave trouble in each by the occasional melting of the cement used in holding the parts together. The same trouble was experienced when the platinum wire of the Wehnelt tip was allowed to project more than about 6 mm. from the tube in which it was mounted. Of course direct current could be used equally well for exciting the Wehnelt interrupter.

The amount of control resistance which it is desirable to use in the primary circuit depends somewhat upon the length of tip used in the interrupter. Thus with 7.1 ohms of control resistance in the primary circuit, a 2 mm. tip gave better deflections than one of 10 mm., but with 4.4 ohms a 10 mm. tip gave the better effect. On the whole the best results were secured with the tip about 4 mm. long and with about 5 ohms of control resistance. The amount of effect caused by varying the resistance step by step with a fixed length of tip (4 mm.) is shown in Fig. 2.

The regularity of action that can be secured with the conditions right is illustrated by the following series of ten deflections taken in succession:

| mm. | mm. |
|---|---|
| 334 | 345 |
| 331 | 347 |
| 331 | 355 |
| 345 | 347 |
| 332 | 347 |

In this case 4.4 ohms of control resistance was used with the Wehnelt tip 10 mm. long.

The circulation of oil through the Righi exciter is a practically important feature, as it keeps the apparatus cool and prevents the irregularities in action which excessive carbonization of the oil would cause. This flow of oil is secured by drawing out the end of a long thistle-tube to a fine point and bending the tube to such a shape that it can be firmly held by a clamp to the upper edge of the frame of the parabolic mirror in which the exciter is mounted. It was adjusted to deliver about 30 drops of oil per minute to the vicinity of the central spark-gap. This construction is shown in Fig. 3. A constant-level overflow tube came up through the small oil chamber of the exciter to a height slightly above that of the spark-gap. After trying vaseline oil, olive

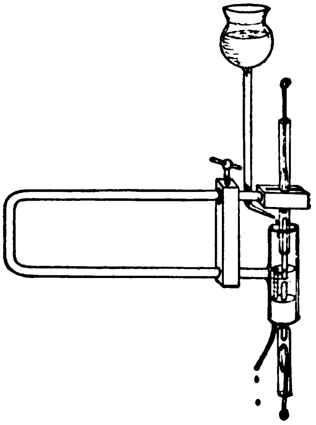

Fig. 3.

oil and lubricating oils of various degrees of viscosity, I have settled down upon ordinary refined petroleum (kerosene) as best adapted for use in exciters of short wave length.[1]

A Caldwell interrupter consisting of two vessels of acid with a small hole in a slate diaphragm between them was also tried, but proved inferior to the Wehnelt interrupter above described.

## APPLICATION TO DEMONSTRATION PURPOSES.

This reduction of the necessary galvanometer sensitiveness to about one-twentieth of its former value makes the thermoelectric receiver for electric waves thoroughly practical for demonstration purposes, and its strictly quantitative character gives it an advantage over other indicators in use. The want of a suitable apparatus for demonstrating the optical analogies of electromagnetic radiation in class and lecture room has been seriously felt by many and the hope of securing it was the primary object of these experiments. Hertz's classic apparatus, so much used in Germany, is too cumbrous, its sensitiveness is small and its indications can be seen by only a few persons at once. The introduction of the coherer enabled Bose,[2] Lodge,[3] and others to reduce the apparatus to convenient dimensions, but this receiver is not strictly quantitative and it is very sensitive to all sorts of disturbing influences. The use of "copper hats" and small diaphragms to shield the coherer from side disturbances undoubtedly change materially the character of the radiation which is being studied. The mirror-strip receiver of Righi is obviously unsuited to demonstration purposes.[4]

The apparatus here described has been found as the result of considerable experience to be well suited for demonstrations and I will close with a few illustrations of its usefulness in this direction.

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[1] To make an actual test of the magnitude of the results obtained with this Wehnelt interrupter in comparison with those secured with the ordinary type, two series of readings were taken, all the conditions being the same in each except that in the first the vibrator furnished with the induction coil was used (a Ritchie 4-inch coil with vibrating hammer interrupter) while in the second the Wehnelt interrupter was employed in its place. The mean galvanometer deflection in the first series was 9.2 mm. but in the second 96.1, or 10.4 times as much with the Wehnelt as with the ordinary interrupter. (Footnote added April 2, 1906.)

[2] Bose, J. C., Proc. Roy. Soc., 160, 167.

[3] Lodge, O. J., The Work of Hertz, etc., p. 32.

[4] Righi, A., Mem. R. Ac. Bologna, 1894. Phys. Soc. Abstracts, 1897, No. 196.

A wave-length of 15 cm. has proved to be well adapted for demonstration. To secure this the total length of the two cylinders in the exciter should be 5 cm. and in the receiver 6 cm. The receiver is shown in Fig. 4. It is a special thermo-couple described more fully in Physical Review, Vol. 20, p. 268. For most purposes both exciter and receiver are mounted at the foci of parabolic mirrors of sheet metal having an aperture about 35 × 35 cm., and placed from one to two meters apart.

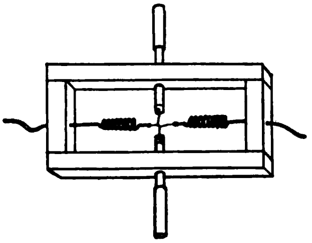

Fig. 4.

I have found it convenient to mount the receiver at the end of a revolving arm about 75 cm. long, swinging in the horizontal plane about a pivot half-way between exciter and receiver. This arrangement constitutes a spectrometer for electric waves.

All the experiments described in the culminating paper of Hertz's classical '87–'88 series[5] (and many others) are readily shown with this apparatus. For a plane reflector a sheet of metal 15 cm. square suffices, but it is better to use one 30 cm. square. A sheet of tin foil allows several per cent. of the radiation to pass through it, while ordinary sheet zinc transmits none. For a prism I use one of 30° angle and having faces 30 cm. square, cast in a wooden form with melted resin. Also a hollow one of glass plates filled with oil. My polarization grating is made of strips of tinfoil 2 mm. wide, 1 cm. apart on a sheet of cardboard. I am making a diffraction grating of tinfoil strips 12 cm. wide with 12 cm. spaces between them. For diffraction experiments I remove the parabolic mirror from behind the linear receiver and still have reasonably large deflections. (The multiplying power of the mirror is 6 to 8 fold.) For a concentrating lens I use an ordinary 5-pint acid bottle filled with benzine. Kerosene or gasoline will answer, but neither seems to be as good as benzine. Placing such a lens before a receiver will increase the radiation received about 5-fold. Stationary waves are formed readily in several ways, as by perpendicular reflection from a plane mirror behind the receiver, or by a similar mirror behind the exciter, or by Boltzmann's two-mirror method.[6] I have given examples of curves showing the maxima and minima obtained by the first two methods in an earlier paper.[7] I add in Fig. 5 an example of the first method named.

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[5] Hertz, H., Wied. Ann., 36, 769, '88.

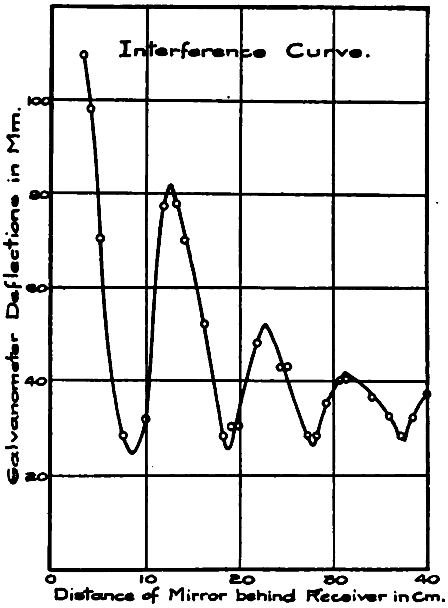

Fig. 5.

These illustrations suffice to show some of the uses of the apparatus and the results that can be obtained. Taking into consideration its comparative handiness, the ease with which its indications can be projected before a large class and the quantitative character of the results obtained, it seems to be adapted for demonstration purposes as well as for research.

Physical Laboratory, Ohio State University,
January 1, 1906.

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[6] Boltzmann, L., Wied. Ann., 40, 399, 1890.

[7] Cole, A. D., Phys. Rev., 20, 270, 1905.

# ON THE MEASUREMENT OF THE REFRACTIVE INDEX BY THE INTERFEROMETER.

By C. A. Proctor.

IN the paper published under the above title in the June number of this journal the authors seem to have lost sight of a source of serious error. When the two paths of light in any interference apparatus are made unsymmetrical by the introduction of a lamina of a dispersive medium into one of them, the central or achromatic fringe of the white light system no longer represents zero path-difference between the interfering rays but is determined by the condition

$$\frac{d\varphi}{d\lambda} = 0,$$

where $\varphi$ is the phase difference between two "congruent" rays, and $\lambda$ the wave length. This causes an increase in the apparent shift due to the introduction of the lamina, and the value of the index obtained from the fringe-count will be too large. This fact was first pointed out I believe by Sir. G. G. Stokes. The theory may be found developed in detail in Preston's "Theory of Light" and other standard works. The error due to this amounts to about 1.3 per cent. in the case of crown glass and increases with the dispersive power of the medium. It is therefore much too large to be disregarded.

It might be noted also that the method employed in measuring the thickness of the laminæ is subject to a theoretical error due to the relative phase change introduced between two rays which have undergone reflection at a glass-silver and an air-silver surface respectively. This error would however be very small if the lamina were of any considerable thickness, and could in any case be easily allowed for.

University of Missouri,
June 27, 1906.

# PROCEEDINGS

# OF THE

# AMERICAN PHYSICAL SOCIETY.

## COEFFICIENT OF LINEAR EXPANSION AT LOW TEMPERATURES.[1]

By H. G. Dorsey.

IN all previously recorded methods of determining the coefficient of linear expansion below about 200° absolute temperature it has been necessary to apply more or less corrections to get the final results or else there has been a possible doubt about the method.

In the present experiment there are no corrections.

The specimen to be examined, a hollow cylinder about a centimeter in length, is placed in a small steel box closed at the top with a glass window and is then carried through the range of temperature from 373° down to 93° absolute. Heat is supplied by a Bunsen burner, or extracted from the box by liquid air. Heating or cooling is so perfectly under control that the temperature may be maintained practically constant at any point between these limits.

The expansion or contraction of the specimen is measured by interference bands of green mercury light. The cylinder rests upon a plate of black glass and supports a plane wedge of glass. Since interference takes place by reflection from the top of the black glass and the bottom of the wedge no compensation is necessary. The air is exhausted from the box so there is no change in wave-length. Consequently each black band counted means an actual change in the length of the specimen of one half the wave-length of the light used.

Temperatures are measured by a copper resistance thermometer which has shown no change in its ice temperature resistance after a year's use. It was calibrated in steam, ice, liquid oxygen and liquid nitrogen.

The coefficient of expansion is measured for temperature ranges of 20°. This short interval brings out peculiarities which have been but little emphasized by previous workers.

Four substances have been studied, principally at the lower temperatures.

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[1] Abstract of a paper presented at the Ithaca meeting of the Physical Society, June 29–July 3, 1906.

The coefficient curve for gold between 93° and 293° has eight points of inflection; maxima occuring at 122°, 198°, 218° and 255° and minima at 142°, 207°, 234° and 272°. The most sudden change is from 0.0000166 at 208° to 0.0000144 at 234°. To check the values at these sudden changes temperature intervals were made 10° as well as 20°. The mean coefficient between 93° and 273° is 0.0000131.

Copper gives a fairly regular curve, dropping from 0.0000162 at 283° to 0.0000104 at 103°. The curve has a slight convexity towards the temperature axis between 170° and 220° while the rest is concave, but there are no points of inflexion. The mean coefficient between 93° and 273° is 0.0000142.

Silver has maxima at 203° and 262° and a minimum at 226°; otherwise a general decrease from 0.0000199 at 283° to 0.0000139 at 103°. Mean coefficient between 93° and 273° is 0.0000166.

Flint glass (tubing) has a principal maximum at 223° and a slight one at 344°. At four places the coefficient remains nearly constant: 170° to 200° it is about 0.0000071, 240° to 260°, 0.0000083, 280° to 300°, 0.0000091, 340° to 374° 0.0000099. Value at 103° is 0.00000505. Mean coefficient between 93° and 373° is 0.00000778.

The work will be extended to a large number of substances including alloys.

## The Temperature of the Moon.[1]

By Wm. W. Coblentz.

FROM his Mount Whitney observations Langley concluded that the soil of an airless planet at the moon's distance from the sun would have a temperature not greatly above — 225° C. His later observations on the radiation from the moon led him to conclude that the temperature of the sunward surface of the moon is about 0° C. His radiation curves rise from a zero value at 6 to 7 $\mu$ to a maximum at 8.6 $\mu$, with a smaller maximum at 10 $\mu$. He found also direct radiation from the sun in this region. The observations on the radiation from the moon during an eclipse show a drop of intensity from a maximum to a minimum in about 1.5 hours, which would seem to indicate that the observed radiation is reflected from the sun since the lapse of time is so short.

The writer has examined the infra-red reflecting power of a series of minerals including quartz, feldspars, amphiboles and micas, which are the chief constituents of the earth's crust, and has found the reflecting power to be practically zero for the region of the spectrum up to 8 $\mu$, followed by bands of metallic reflection from 8.5 to 10 $\mu$. In this latter region the mean reflecting power is from 40 to 50 per cent. for the silicates, while pure quartz has a reflecting power of 90 per cent.

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[1] Abstract of a paper presented at the Ithaca meeting of the Physical Society, June 29–July 3, 1906.

It follows, therefore, that the earth and the moon may be considered selectively reflecting surfaces with a band of metallic reflection from 8.5 to 10 $\mu$. The radiation from the sun is so much more intense than that of the moon that, with a reflecting power of 50 to 90 p.c. at 8 to 10 $\mu$, one would expect the amount of reflected energy to be, at all times, greater than the direct radiation from the moon.

The results as a whole show that it is just as reasonable to consider the radiation from the moon at 8.5 to 10 $\mu$ to be reflected from the sun as to consider it due to a temporary rise in temperature of the sunward side of the lunar surface, and Langley's first conclusions of a lunar temperature of — 225° C. again obtains.

WASHINGTON, D. C.,
June 15, 1906.

## INFRA-RED REFLECTION SPECTRA.[1]

BY WM. W. COBLENTZ.

THE examination includes metals (*e. g.*, Zn, Cd, Pd) and sulphides of metals. The reflecting power of the sulphides of Zn, Fe and Sb are worthy of notice. They are known for their metallic lustre, especially stibnite, $Sb_2S_3$. The reflecting power of pyrite, $FeS_2$, rises from 20 per cent. at 1 $\mu$ to 35 per cent. at 14 $\mu$ and in its general trend is similar to that of iron. Sphalerite, ZnS, reflects only about 8 per cent. throughout the spectrum to 14 $\mu$. Stibnite is the most extraordinary in having a reflecting power of about 37 per cent., to 12 $\mu$. A section 0.4 mm. thick transmitted, on an average, about 46 per cent. throughout the spectrum, while a section 4.9 mm. thick transmitted 43 per cent., which after correcting for surface reflection indicates that the true absorption is only some 2 or 3 per cent. Such a great transparency has been found in but few substances except gases.

The refractive index of stibnite found by Drude for sodium light is $N = 4.49$ (5.17). The value calculated from the well known Fresnel formula, using the reflecting power for the region from 4 to 8 $\mu$, gives a value of $N = 4.72$, and $N^2 = 16 +$, while the observed dielectric constant is only about 10. Evidently there is something wrong in the assumption that stibnite is a homogeneous non-conducting medium.

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[1] Abstract of a paper presented at the Ithaca meeting of the Physical Society, June 29–July 3, 1906.

## NOTE ON THE GRAPHICAL REPRESENTATION OF NON-SINUSOIDAL ALTERNATING CURRENTS.[1]

BY FREDERICK BEDELL.

THE current in an inductive circuit without iron lags ninety degrees behind an impressed sinusoidal E.M.F. and is itself sinusoidal. In the graphical representation, the current is represented by a line at right angles to the line which represents the E.M.F., these two lines determining a plane.

Iron causes a hysteresis loss and harmonics. The hysteresis loss introduces a power component of current of fundamental frequency, so that the total fundamental component of the current is advanced in phase, remaining in the plane of fundamental frequency.

The harmonics are wattless and hence are in quadrature to the E.M.F. It can be shown that graphically they are also in quadrature to the fundamental component of current, and accordingly are represented by a line at right angles to the plane of fundamental frequency.

## THE CALIBRATION OF CAPILLARY TUBES.[1]

BY WILLARD J. FISHER.

IN connection with researches on the viscosity of gases, H. Schultze[2] has described a method of calibrating tubes based on the combined use of long and short mercury threads. The following method, suggested by his, differs in the adoption of a graphical reduction, and a greater number of measurements. It is adaptable to calibrations for any purpose.

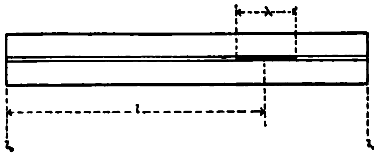

Fig. 1.

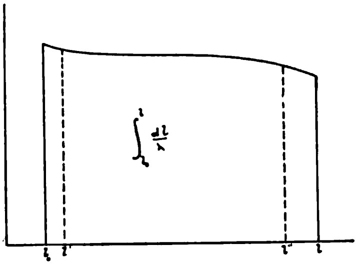

Fig. 2.

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[1] Abstract of a paper presented at the Ithaca meeting of the Physical Society, June 29–July 3, 1906.

[2] H. Schultze, Ann. d. Physik, 5, p. 147, 1901.

I. *For Volumes.* — From any arbitrary position (in practice marked by etching the tube) designated by $l_0$, measure the position $l$ of the center of a *short* mercury thread, also the length $\lambda$ of the thread (Fig. 1). At the point $l$ the cross-section of the tube is $Q = V/\lambda$, very nearly, in which $V$ is the volume of the thread. Measured from $l_0$ the total volume of the tube to $l$ is $v - v_0$. Also $dv = Qdl = V/\lambda dl$. If $V$ is kept constant by temperature control,

$$v - v_0 = V\int_{l_0}^{l}\frac{dl}{\lambda}.$$

Plot a curve with $y = 1/\lambda$, $x = l$. Its area

$$= \int ydx = \int_{l_0}^{l}\frac{dl}{\lambda} = \frac{v - v_0}{V}.$$

If the cross-section of the tube is small the volume of the short thread cannot be computed accurately from weighings, since the container must be of greater mass than the mercury itself. Hence a more accurate way to find $V$ is to find the total volume of the tube by a *long* thread between two points $l'$ and $l''$. Call this volume $v'' - v'$. Then

$$V = \frac{v'' - v'}{\int_{l'}^{l''}\frac{dl}{\lambda}},$$

and is determined in terms of known quantities.

For thermometers the integral

$$\int_{l_0}^{l}\frac{dl}{\lambda}\ .$$

can be taken between the limits given by the steam and ice points, and its value equal to 100° ; then the intervening points may be interpolated.

II. *Viscosity Tubes.* — The current of fluid is proportional to $r^4/l$, for uniform tubes, therefore to $1/(l/r^4)$. For nonuniform tubes put the sum of the quantities $l/r^4$ equal to $F$, which is then proportional to the resistance experienced by the fluid ;

$$F = \Sigma\frac{l}{r^4} = \int\frac{dl}{r^4}.$$

Assuming the cross-section circular, $Q = \pi r^2 = V/\lambda$

$$\therefore \frac{1}{r^4} = \frac{\pi^2}{V^2}\lambda^2$$

and between the limits $l_0$ and $l_1$,

$$F_1 - F_0 = \frac{\pi^2}{V^2}\int_{l_0}^{l_1}\lambda^2 dl.$$

Plot a curve with $y = \lambda^2$ and $x = l$. $V$ is known from the curve for volumes; then $F_1 - F_0 = \pi^2/V^2$ into the area under the curve between the limits $l_1$ and $l_0$.

This theory can evidently be extended to calibration for other functions of the radius.

In practice it is advisable to run the thread through the tube more than once, as the points on the curve of one run may not exactly coincide with those for another.

## THE PRODUCTION OF OZONE BY A PHOTO-ELECTRIC CURRENT IN OXYGEN.[1]

BY HARRY S. HOWER.

ULTRA-VIOLET light was allowed to fall upon a polished platinum knob in an oxygen atmosphere.

The knob being changed to about — 1,500 volts, the discharge current from it to the earthed wires opposite it was measured by a galvanometer in series. The ozone produced was detected by its effect on a piece of platinum foil. The foil changes its position in the voltaic series when it absorbs $O_3$.

## NOTE ON ELECTRIC DOUBLE REFRACTION IN CARBON-DISULPHIDE AT HIGHER TEMPERATURES.[1]

BY L. B. MORSE.

AT a former meeting of the Physical Society the late D. B. Brace reported that he had not been able to observe the "Kerr effect" in air. A beam of plane polarized light showed no trace of ellipticity after passing back and forth several times in the air between long charged plates.

Schmidt's curve, for the effect of temperature on the Kerr effect in $CS_2$, shows a more rapid rate of decrease of the effect with increase in temperature, at the higher than at the lower temperatures at which he worked.

At the time this work was begun an apparatus was being constructed in which ordinary gases, gaseous $CS_2$, etc., were to be tested under varying conditions of temperature and pressure.

In view of the above and other considerations it seemed important to see whether or not there was a great decrease in the effect at temperatures nearer the boiling point.

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[1] Abstract of a paper presented at the Ithaca meeting of the Physical Society, June 29–July 3, 1906.

Next to the difficulty of keeping constant and uniform temperature throughout the tube the greatest obstacle to be overcome was to keep the ends of the tube containing the hot $CS_2$ closed with cover glasses free from strains.

Cover glasses (free from double refraction) were cemented with thin water glass over holes drilled in thick plate glass. The larger part were spoiled in drying. Two of the more perfect were held by springs firmly against the ground glass ends of the tube, and the joint wrapped with twine soaked with water glass.

Readings taken at 24.4° and 41.6° would fit nicely on an extension of Schmidt's curve — showing that there is no marked change in the rate of decrease of the effect.

Certainly there is nothing in the behavior of $CS_2$ under electric strain at this temperature which would lead one to expect the effect to be zero at the boiling point, or in the gaseous state.

# ELECTRIC DOUBLE REFRACTION IN CARBON DISULPHIDE AT LOW POTENTIALS.[1]

BY L. B. MORSE.

WHAT is known as Kerr's law of double refraction (which has been verified by later investigators, using high potentials) may be written as follows:

$$\delta = B\frac{P^2}{a^2}l,$$

where $B$ is a constant depending upon the dielectric, $l$ the length and $a$ the distance between the plates, $P$ is the difference in potential between the plates. From PHYSICAL REVIEW (paper by Elmen), January, 1905, "there seems to be a decided variation from the above law for low potentials."

The variation of the points on the curve published was naturally rather large near the limit of sensibility. Knowing that several improvements had increased the sensibility of the apparatus an effort was made to determine the curve more accurately if possible. Readings could be taken at lower potentials, and with less error at the same potentials used in the above investigation.

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[1] Abstract of a paper presented at the Ithaca meeting of the Physical Society, June 29–July 3, 1906.

In order to obtain more accurate results observations were repeated till the eye became strong enough to take readings for a whole curve from lowest to highest potentials in a very short time. The effect at the lowest potentials was measured first — then up to the higher, where the eye could read to a greater relative accuracy than at the lower potentials even when very tired.

After entirely changing the parts of the apparatus and readjusting, the same results (approximately) were obtained.

*All the results obtained indicate that Kerr's law holds* within the range of probable experimental error.

A large part of the increased sensibility is without doubt due to a direct-connected filter system, and the *better* nicol prisms used, and perhaps in part to the more symmetrical position of the "dividing line" used in matching.

## THE PRODUCTION OF OZONE BY BECQUEREL RAYS PASSING THROUGH OXYGEN.[1]

BY HARRY S. HOWER.

VARIOUS methods of detecting the cause of the ozone odor observed near radium capsules in air were unsuccessful. By the delicate method of the preceding abstract, the attempt was made to show which rays change $O_2$ to $O_3$. No effects were observed for $\beta$- and $\gamma$-rays. The $\alpha$-rays gave a decided positive result.

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[1] Abstract of a paper presented at the Ithaca meeting of the Physical Society, June 29–July 3, 1906.

# NEW BOOKS.

*Avogadro and Dalton — the Standing in Chemistry of their Hypotheses.* By ANDREW N. MELDRUM, D.Sc. Pp. 113. Edinburgh, James Thin, 1906.

The book consists of two essays, dealing with the present standing and relative importance of the hypotheses of Avogadro and Dalton. The author, whose position is sometimes more that of an advocate than of a judge, holds that the present importance of the former is the greater. After careful and critical study of the original papers and the meanings of the hypotheses to the two great originators themselves, he concludes that Avogadro's molecule is practically that to which present-day chemists are accustomed; while Dalton's atoms were rather unfruitful conceptions, never resulted in the evolution of order from the chaos of chemical facts accumulated during the first half of the nineteenth century, and are now in reality superseded.

The first essay, of seven chapters, shows in order that Avogadro developed his hypothesis as an explanation of Gay-Lussac's law of the simple volume ratios which are observed in the combination and decomposition of gases — then not with special reference to the laws of Boyle and Charle, which is contrary to common impression; that the deduction of Avogadro's hypothesis from the kinetic theory of gases might well be reversed, and the usual assumption of the identity of thermal and kinetic equilibrium among the gas-molecules might as well or better be deduced from Avogadro's hypothesis; that molecular weights are always deduced on the assumption of the hypothesis, as applied to gases or liquids; that in the determination of atomic weights doubtful cases are always settled by reference to the hypothesis, or by analogies with cases where it can be applied, and that other hypotheses which conflict with it are invariably discarded; that the accepted ideas of valence and the molecular formulas of the elements $H_1$, $O_2$, $O_3$, $P_6$, etc., are due to this hypothesis; and that "purely chemical methods" — meaning, no doubt, purely *gravimetric* methods, — do not suffice even to determine the formula of water. To quote from p. 49, Avogadro's hypothesis "is the basis of our knowledge of molecules and radicals and atoms. Molecular weights being ascertained, and then atomic weights, the periodic system becomes possible. The chief issues of the hypothesis are the molecular theory, including the modern theory of solution, the atomic hypothesis, the doctrine of valency, and the periodic system — the last a perpetual source of speculation and experiment."

The second essay, also of seven chapters, begins with the attempt to extract from Dalton's words the meaning to himself of his hypothesis, and to compare with this the modern ideas of it; concluding that it was an essentially gravimetric explanation of matter, whose author not only did not accept Avogardo's view, in the form which Dalton himself had imagined it, but also rejected Gay-Lussac's experimentally derived law; and that modern Daltonians hold theories of a mixed gravimetric and volumetric nature very different from anything that Dalton himself believed. It proceeds with short expositions of the chemical systems of Berzelius, Gmelin and Gerhardt and Laurent, and states (p. 96) that in 1850 to 1860 at least five symbols for water were in use, HO, $H_2O$, O, $H_2O_2$, $O_2$; for acetic acid "there were formulæ in bewildering profusion"; and further, that according to his school, $H_2O_2$ might mean to the chemist water or hydrogen peroxide; $C_4H_4$, marsh-gas or acetylene; $C_4H_4O_4$, acetic acid or fumaric acid; CuCl, cuprous or cupric chloride. From this state of confusion we were delivered by the writings of Cannizzaro, published in 1858, forty-seven years after Avogadro's first paper, and made widely known in 1860. He had studied the accumulated data on the vapor-density of inorganic substances, and consistently applied to the subject the hypothesis of Avogadro, with the result of an atomic weight system which was universally accepted within four years, and has stood to this day with only such changes as would be brought about by refinements of analysis; where the old chemists differed about magnitudes of hundreds of per cent., the modern analyst makes changes of tenths or hundredths of per cent. In 1865 appeared Newlands' "Law of Octaves," the first of the forms of the periodic law, all of which, together with the doctrine of valence, were impossible under any former atomic weight system.

Whatever the actual meaning of Avogadro's hypothesis, it has fulfilled in high degree the condition which Mach has proposed, that acceptance of a doctrine is based upon the degree of economy of mental effort which it produces. And to the expression of the hope that others may obtain from the reading of Dr. Meldrum's little volume as much pleasure and profit as he, may the reviewer add that it might be well to follow the author's suggestion and make this hypothesis, so fundamental in chemistry, a chief prop instead of a mere side issue in the teaching of the Kinetic Theory?

W. J. Fisher.

*Handbuch der Pkysik.* WINKELMANN. (Zweite Auflage.) Leipzig, J. A. Barth. 1903.

In the second edition of Winkelmann's "Handbuch" the plan of the original work has been continued and greatly extended. The new edition is to consist of six volumes in place of the three volumes of the original work and a number of specialists have been added to the original staff of contributors. The subject of Sound, which in the first edition was treated, in Volume I., as a special part of mechanics, is given a volume to itself. The treatment of Electricity is extended to cover two volumes and Optics which was contained in Volume II. of the first edition is placed at the end of the work and appears as Volume VI.

The new edition is in no respects a revision of the first but consists of a series of entirely new monographs or treatises written by specialists in each department and bringing the subject up to date. Among the new contributors to the volumes on Electricity are Luther on "Electrolysis," Stark on "Electricity in Gases and Radioactivity," Gerdien on "Atmospheric Electricity," Cantor on "Voltaic Cells and Storage Batteries," and Duden on "Contact Electricity." In the first part of Volume VI. the work of Czapski on "Geometrical Optics" is supplemented by chapters on "Vision" and on "Photographic Objectives" written by von Rohr. There is likewise a chapter on "Apparatus for Projection" by Eppenstein.

The method followed in the production of Winkelmann's "Handbuch" gives it a place distinct from that of other general treatises on Physics. It does not supplant these but supplements them in an admirable manner and each edition supplements instead of supplanting the one that went before. At the time of writing this notice Volumes I., II., III., the second part of Volume V. and the second part of Volume VI. had not yet been received. A review of these will be given at a later day.

*Volume XXIII.* *October, 1906.* *Number 4.*

# THE

# PHYSICAL REVIEW.

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## ON THE REFLECTION AND TRANSMISSION OF ELECTRIC WAVES BY SCREENS OF RESONATORS AND BY GRIDS.[1]

By F. C. Blake and C. R. Fountain.

### 1. Introduction.

EXPERIMENTS on electrical resonance for linear strips of metal have been conducted in a number of ways. Garbasso[2] worked with the reflection of electrical waves from wooden walls covered with linear resonators, parallel and uniformly distributed. He found that there was a selective absorption of the waves, getting high reflectivity when the resonators were in tune with the vibrator and then only. Garbasso and Aschkinass[3] measured the deviation of electrical waves through a prism built up of linear resonators on glass plates, the transmitted wave falling on a small parabolic mirror, itself constructed of resonators. They observed that the deviation depended upon the length of the resonators constituting the receiving mirror. Thus they found that both the refraction and the absorption decreased with increasing wave-length. Aschkinass and Schaefer[4] measured the transmission of electric waves through screens of resonators both when in air and when immersed in certain liquid dielectrics. In this way they obtained the refractive indices of the dielectrics for the wave employed.

[1] Read before the American Physical Society, Oct. 28, 1905.

[2] Garbasso, Atti Acc. di Torino, Vol. XXVIII., pp. 470 and 816, 1893. Journal de Physique, Vol. 22, p. 259, 1893.

[3] Garbasso and Aschkinass, Ann. der Physik, Vol. 53, p. 534, 1894.

[4] Aschkinass and Schaefer, Ann. der Physik, Vol. 5, p. 489, 1901.

The present experiments were undertaken at the suggestion of Professor E. F. Nichols with the view of studying more completely than hitherto the passage of electric waves through systems of linear resonators and, if possible, to throw further light on the question of the relation between the length of the wave and its corresponding resonator-length.

## 2. Apparatus and Wave-length.

*Vibrator.* — The vibrator was of the customary three-gap or Righi type placed in the focal line of a cylindrically parabolic mirror. It consisted of two brass balls (*BB*, Fig. 1), each 0.952 cm. in diameter, sparking in olive oil, the lead-in copper wires forming the air gaps *AA*. The two auxiliary spheres were two knobs of 0.15 cm. diameter fused on the ends of the lead-in wires. They were made small in order to disturb as little as possible the characteristic vibration of the two principal spheres. By means of sealing-wax the two balls *B*, *B*, were attached to glass tubes, through which the lead-in wires passed. To avoid line effects these wires were drawn through an opening in the mirror directly behind the vibrator and brought out as close together as non-sparking would allow. The air-gaps *A* and *A*, were usually about 0.4 cm. long. The whole was surrounded with a glass reservoir *G* for oil, provided with suitable inlet and outlet tubes (not shown) and fitted with rubber corks through which the glass tubes led. Back of the mirror these tubes were attached to a thumb-screw arrangement by means of which the length of the spark-gap *O* in oil could be altered at will. The efficiency of the vibrator was found to be a maximum when the balls were all but touching, *i. e.*, when the length of *O* was a very small fraction of a millimeter.

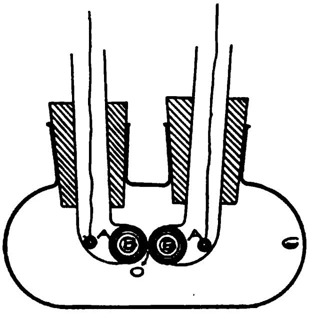

Fig. 1.

The source of energy was a 10-inch induction coil, with interrupter and condenser removed, connected to a 110-volt 60-cycle alternating-current circuit. In this way the use of an interrupter, so frequently unsatisfactory, was avoided. The current in the primary was reduced to 7 amperes by suitable resistance in circuit.

Early in the work it was found that the oil surrounding the spark gap hindered the escape of the decomposition gases due to the spark. The axis of the vibrator was therefore changed from the vertical to a horizontal position and a constant stream of oil was led through the chamber *G*, entering below the spheres *BB*.

*Receiver.* — The wave detector was of the Klemenčič type, differing from the form used by Willard and Woodman[1] only in minor details. The diameter of the iron and constantan wires used was 0.0025 cm. These wires were soldered to copper strips 2 mm. wide fixed on wood and then they were crossed and joined to copper wires of larger size leading to the galvanometer. These larger wires were drawn away from the receiver immediately back of the thermal junction, so that no wire was exposed to the waves beyond the width of the copper strips. The total length of both the iron and constantan wires was thus not more than 3 mm. each. All junctions were soldered, as little solder as possible being used on the thermal junction itself so as not to lower too greatly its sensitiveness. This receiver was placed with its length horizontal in the focal line of a second parabolic mirror. The two mirrors were of sheet zinc and of equal aperture 70 cm. across by 63 cm. along the axis. The focal distance was 7.5 cm. A second, or check, receiver was placed directly in front of the sending mirror at a distance of 23 cm. from the vibrator and connected with a second galvanometer. This receiver will be spoken of as the check receiver, and the one in the receiving mirror as the main receiver. The resistance of each was about 2 ohms. As all junctions were soldered the resistance of neither receiver varied appreciably. The receiver resistances were always measured before and after a curve was taken. When, as happened occasionally, anomalous results were obtained in the midst of a curve, checking up the receiver resistances generally revealed an unsoldered or broken junction.

*Galvanometers.* — The galvanometers were of the du Bois-Rubens two coil type, triply ironclad. Owing to the proximity of all sorts of heavy street traffic and varying electric currents from tram and lighting circuits it was found necessary to hang the galvanometers from wall brackets by Julius suspensions and to add additional armor. For the latter purpose sheet iron was employed, five layers being wound spirally, separated from one another by strips of cork-rubber matting. In this way the magnetic disturbances were generally not more than five scale divisions for galvanometer $C$ (attached to check receiver) and three for galvanometer $M$ (main receiver). As the readings for the curves were generally large, some 200 or 300 scale divisions, the error due to these extraneous disturbances was small. The sensitiveness of $M$ was $2.5 \times 10^{-9}$ amperes, $C$ $2.2 \times 10^{-9}$ amperes. With coils connected in multiple the resistance of each galvanometer was about 2.5 ohms.

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[1] Willard and Woodman, PHYS. REV., Vol. 18, p. 3, 1904.

A rather elaborate system of mercury-cup connections was inserted as a key-board between the receivers and the galvanometers to admit of cross connections for reducing the effect of magnetic disturbances by allowing the two galvanometers to be read always in the same direction, and the insertion of suitable shunts to reduce the larger readings to scale limits. The two galvanometers were accurately adjusted to the same period, four seconds for a complete swing. Having once adjusted them to this period they remained so steady it became unnecessary to touch them throughout the course of the work. Readings were obtained by noting the zero position and the first throw. The drift of the zero point was usually slow and so small as to make the reading of return swings unnecessary.

*Tuning of the Receivers.* — For this purpose the two mirrors were placed facing each other in the usual way, their focal lines being horizontal, 1.3 meters above the floor and 2.4 meters apart. To prevent air currents affecting the thermal junctions the apertures of both mirrors were covered with thin card-board and each receiver was surrounded by a small paper box.

By a preliminary experiment the check receiver had been shortened to a length of 3.5 cm. and it was kept constant at this length during the shortening of the main receiver. The tuning of the latter is plotted as a curve in Fig. 2. Abscissas are total lengths of the receiver in centimeters; ordinates, the ratios $M/C$ of the galvanometer deflections. It is to be noted that the curve gives multiple tones of the receiver, minima at even, and maxima at odd multiples of the fundamental length. This is as it should be, for the current in the receiver is a maximum when there are loops of potential difference at its ends. So far as it was carried the curve agrees with curves 1 and 2 obtained by Willard and Woodman.[1] Their curves show the harmonics of the vibrator but not the multiple tones of the receiver, for they did not start with sufficient lengths to show these.

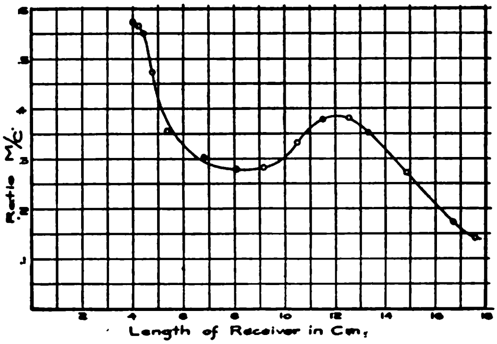

Fig. 2.

By trial it was found immaterial whether the check receiver was tuned — for some of the work it was kept at the length 3.5 cm.; later it was changed to the proper resonance length, 4.0 cm.

*Deterioration of the Vibrator.* — Although a check receiver was employed to take account of the irregular action of the vibrator, it was found that, starting with the vibrator in a new and fresh condition, the ratio $M/C$ gradually lessened as the spark gap deteriorated. In addition to the constant eating away of the material of the spheres a filament of carbon from the decomposed oil would gradually bridge the gap, both causes tending to lessen the radiation. By making and breaking the circuit a few times this bridge could be torn away and the galvanometer readings immediately following its disappearance were invariably very large. Before this unsatisfactory condition of the vibrator was reached, however, it was generally renovated. To do this it had to be taken all apart, because the construction and the small size of the balls prevented the possibility of turning new portions of the spheres into position for sparking by merely rotating the glass tubes to which they were attached. In all cases the vibrator was not touched during the progress of any one set of readings although tests were made which showed that any measurement could be duplicated to within 5 per cent. after the vibrator had been removed, readjusted and replaced. The ordinary duplication for any curve-point, obtained by simply repeating readings was usually within 2 per cent.

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[1] Willard and Woodman, l. c.

The following sample series of figures illustrates the decrease in the ratio $M/C$ as the condition of the vibrator grew poorer. Each figure is the mean of seven readings, successively taken under constant conditions; 0.804, 0.802, 0.798, 0.784, 0.790, 0.784, 0.776, 0.764, 0.777, 0.768, 0.754, 0.750, 0.741, 0.740, 0.732, giving a total variation of 9 per cent. Moreover, the series shows that the falling off is somewhat irregular. Now it was found that an increase in the length of the spark gap $O$ invariably produced a decrease in the energy radiated and a corresponding decrease in the ratio $M/C$. In general, it would seem that the violent action to which the vibrator was subjected, together with the constant wearing away of the brass spheres gradually lengthened the gap; and yet at any one instant a projecting particle of brass might easily have shortened it for the moment, thus accounting for the irregularity in the decrease of the ratio.

But however irregular the vibrator's action, due to *any* cause, one would expect the ratio $M/C$ to hold constant, provided both receivers wese sufficiently far removed from the vibrator as to be affected by *pure* radiation only. The observed decrease in this ratio indicates that the check receiver, distant from the vibrator 23 cm. or a little more than two wave-lengths, was close enough to receive some of the energy that periodically flowed back into the vibrator. Since these two portions (the *pure* and the *impure*) of the radiation which reaches the check receiver do not vary proportionally, for a small amount of energy emitted by the vibrator the denominator of the fraction would be relatively too large.

Instead of removing the check receiver to a greater distance it was easier to eliminate as far as possible all irregularity in the vibrator's action in the following way: Whatever varying system was being measured, readings of a second constant system were alternately taken, giving a second ratio $M'/C'$. The quotient $\frac{M/C}{M'/C'}$ should not contain any effect of irregularity in the vibrator's action. For example, suppose one was measuring the transmission of energy through a system of resonators as their length was gradually shortened. He could take alternate readings of the transmission through air, obtaining a second ratio $M'/C'$, and thus eliminate various irregularities.

*Measurements of the Wave-length.* — For measuring the length of the principal wave emitted by the vibrator the interferometer method[1] was employed. The separating surface was a grid of fine copper wire (B. & S., No. 34) mounted on a wooden frame 125 by 100 cm. The distance between the wires was 3 cm. The fixed mirror was zinc, 117 by 95 cm.; the movable mirror was a silvered surface on the front face of a piece of plate glass 122 by 96.5 cm. This silver mirror was supported in one of two equal compartments of a sliding framework, itself encased in another framework arranged to move in the direction of the wave along a set of ways. The

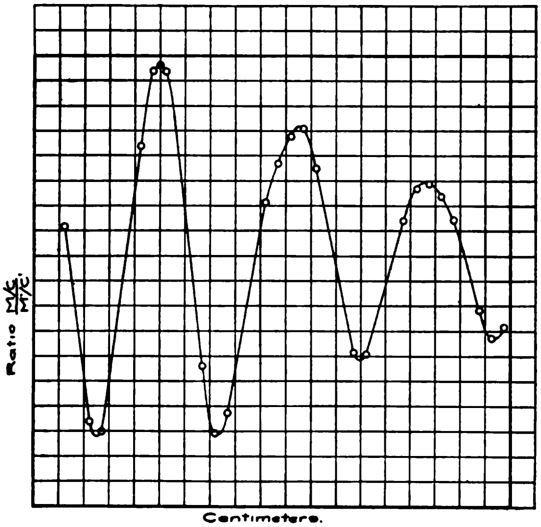

Fig. 3.

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[1] For the advantage of this method see G. F. Hull, Phys. Rev., Vol. 5, 1897, and Willard and Woodman, l. c.

sliding device, by allowing the removal of the silver mirror from the path of the wave, afforded alternate readings of the effect of reflection from a third metal mirror fixed in position back of the movable one. Thus the ratio $M'/C'$ was obtained. The interference curve is shown in Fig. 3, the ordinates being the ratio $\frac{M/C}{M'/C'}$. The complex character of the radiation is shown by the unequal spacing of successive maxima and minima. For estimating the wave-length from this curve only the principal maximum and its two adjacent minima were considered, for it is in the immediate neighborhood of this maximum, where the two plane mirrors are equally distant from the separating surface, that the heads of the two wave-trains combine most strongly. In this way the wave-length came out 9.9 cm. An almost identical curve was obtained by using a separating surface with the wires 1.5 cm. apart. Had the spacing been 2.2 cm. the sharpest maxima and minima possible would have been obtained.

## 3. Resonators in Air.

The energy transmitted and reflected by various systems of resonators in a plane both in air and on glass was measured as their lengths were shortened and the results are plotted as curves in Figs. 6, 8, 9 and 10. All of the useful details as to the distribution of the resonators for the curves shown are collected into Table I. Tinfoil strips 2 mm. wide were employed throughout the work, their length being always parallel to the electric force of the wave, and in its plane for the transmission measurements. The arrangement of apparatus for transmission is shown in Fig. 4 and for reflection in Fig. 5; both diagrams are drawn to scale. The reflecting angle was 12° 45′, with a cosine of 1 approximately. To avoid diffuse

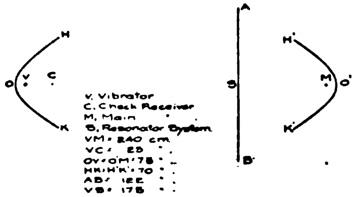

Fig. 4.

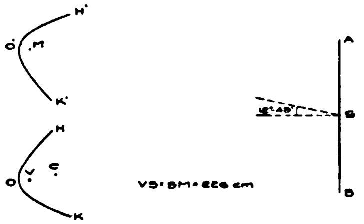

Fig. 5.

## TABLE I.

*Distributions of Resonators.*

| Designation of Curves. | Number of Columns. | Number of Resonators in a Column. | Distance between Columns (Adjacent Edges). | | Distance between Resonators Sidewise (Axially). | Length of Resonators. | | |
|---|---|---|---|---|---|---|---|---|
| | | | At Beginning. | For Resonance. | | At Beginning. | For Resonance. | |
| Fig. 6, *T* and *R*. | 7 | 39 | 1.0 | 5.7 | 3 | 10.0 | 5.3 | Air. |
| " 6, $T_1$. | 13 | 20 | 0.7 | 1.1 | 6 | 5.3 | 4.9 | |
| " 6, $T_2$. | 13 | 12 | 1.0 | 2.6 | 10 | 6.0 | 4.4 | |
| " 6, $T_3$. | 15 | 5 | 1.0 | 1.6 | 20 | 5.0 | 4.4 | |
| " 8, *T* and *R*. | 13 | 39 | 0.5 | 3.5 | 3 | 6.0 | 3.0 | Sheet Glass. |
| " 8, $T_1$. | 7 | 39 | 1.0 | 8.0 | 3 | 10.0 | 3.0 | |
| " 8, $T_2$. | 13 | 23 | 0.5 | 3.2 | 5 | 5.5 | 2.8 | |
| " 9, *T* and *R*. | 13 | 39 | 1.0 | 4.45 | 3 | 6.0 | 2.55 | Plate Glass. |
| " 10, *T* and *R*. | 7 | 117 | 0.5 | 6.0 | 1 | 10.5 | 5.0 | Sheet Glass. |
| " 10, $T_1$. | 7 | 75 | 1.0 | 7.0 | 1.5 | 10.0 | 4.0 | |
| " 10, $T_2$ and $R_2$. | 7 | 59 | 0.5 | 7.7 | 2 | 10.5 | 3.3 | |
| " 10, $T_3$. | 7 | 12 | 0.5 | 8.5 | 10 | 10.5 | 2.5 | |

reflection from the walls of the room the apparatus was arranged diagonally with respect to them.

By a carefully conducted series of tests with a grid of fine wires 5 mm. apart the wave emitted by the vibrator was found to be 100 per cent. plane-polarized. Accordingly it was deemed unnecessary to insert, after the method of Aschkinass and Schaefer,[1] such a grid in the path of the waves. Moreover, a screen to cut off diffraction effects was not used for it was thought that better comparative results for transmission and reflection would be obtained without its use, since in the one case such a screen could not be used. However, to make sure that the diffracted energy was small, a plane metal mirror the size of the resonator system was inserted at *S*, Fig. 4, and the galvanometers read. The effect at *M* was less than 1.5 per cent. of the incident energy. In Fig. 5 such a mirror was inserted in a position close to the vibrator mirror but so inclined as to reflect none of the energy into the receiving mirror. A small effect, 1.4 per cent., was still felt at *M*. In both of these cases the phase relation that this diffracted energy bore to the main portion of the energy was unknown and so it was not corrected for in any of the curves. It shows itself especially in curves *R*, Fig. 6, length 0 cm., and *R*, Fig. 12, distance 8 cm.

In the transmission work, to avoid the possibility of interference effects at the check receiver *C* the resonator system *S*, Fig. 4, was placed relatively close to the receiving mirror. By choosing a resonator system that reflected the larger proportion and yet transmitted some of the energy and by making careful tests as it was moved along the line *VM* (Fig. 4), no effects due to interference could be detected at *C*.

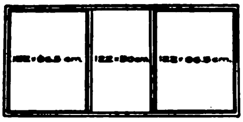
Fig. 5a.

The resonator system *S* was fitted into one of two equal compartments of a sliding framework (Fig. 5, *a*). For the work on transmission through resonators in air the other compartment was left empty; for resonators on glass it was either empty or fitted with a bare glass plate, the duplicate of the one supporting the resonators. For the work on reflection the second compartment held a plane metal mirror, the silver mirror used in measuring the wave-length serving as the check reflector. By sliding *S* back and forth across the path of the waves readings were alternated between the two compartments, giving the ratio $\frac{M/C}{M'/C'}$. Thus the reflection or transmission was measured.

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[1] Aschkinass and Schaefer, l. c.

As a rule only five readings constituted a set for any given length of strips, three of the resonator system under observation and two of the check system; for during the progress of the work it had been found that better results were obtained for a small than for a large number of readings, since in this way excessive deterioration of the vibrator was avoided.

Of the curves in Fig. 6 for resonators in air *T* was taken with the strips attached to cross section paper and *R*, $T_1$, $T_2$ and $T_3$ to tracing cloth. By a previous test both of these substances were found to have an index of refraction of 1 for the wave employed. *R* was the first one of the curves taken and shows that the resonance-length was passed unexpectedly. It was carefully located, however, at 5.3 cm. in the *T* curve. As the mean of *T* and *R*, the dotted curve shows

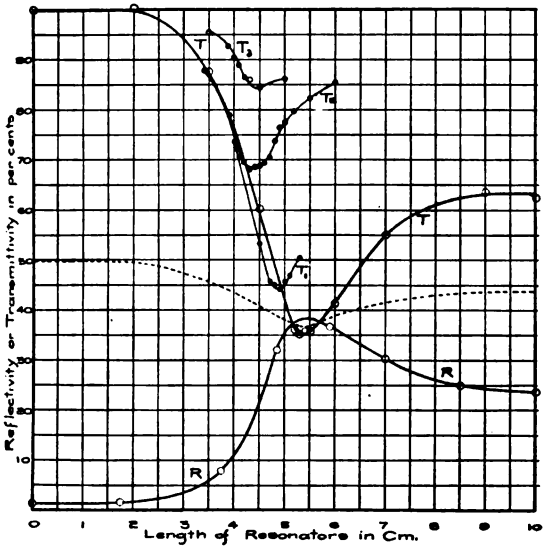

Fig. 6.

that the scattered radiation is a maximum at the resonating length. This agrees with expectation on the assumption that none of the energy suffers degradation. It is seen that when the strips are shorter than 2 cm. or $\frac{1}{5}\lambda$ there is practically no absorption.[1]

It was thought worth while to see what would be the maximum reflection obtainable from a set of resonators of the above length, 5.3 cm., using a more dense distribution. In the work with resonators on glass (to be mentioned later) it had been found that a change in the side-on distance between resonators altered the length for maximum resonance while a change in the end-on distribution, within the limits investigated at least, did not affect it. Accordingly, keeping the side-on distance the same as before, 3 cm., the number of columns was increased from 7 to 13, making the distance between adjacent edges of adjoining columns 0.7 cm. The coefficient of reflection of this set was 79.0 per cent.

Two other distributions of resonators in air were tried — $T_1$, obtained from the set just mentioned by removing alternate horizontal rows, and $T_2$. For $T_1$, with strips 6 cm. apart, resonance occurred at the length 4.9 cm.; for $T_2$, strips 10 cm. apart, at 4.4 cm.

To show the relation between side-on distance and resonating-length the curves in Fig. 6 are summarized in *A*, Fig. 7. It turns out a straight line making an appreciable angle with the axis of abscissas, and shows that the magnetic fields of the resonators do not cease to influence each other until the resonators are nearly a whole wave-length apart. That the resonance-length should decrease with increasing distance between the strips was to be expected; for since

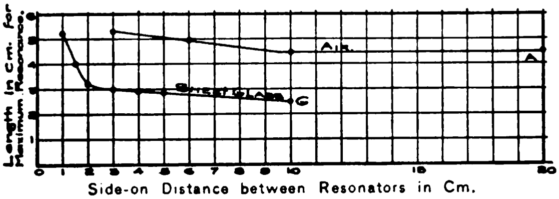

Fig. 7.

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[1] Following Aschkinass and Schaefer the word "absorption" will be used in this paper to mean the diminution in energy in passing through a resonator system; it thus includes reflection, scattering and degradation into heat if any.

at any instant the currents in the resonators are all in the same direction the effect of induction is reduced by decreasing the distance between them; hence in order to respond to a given wave the capacity of the resonators must be increased, that is, they must be lengthened.

### 4. Resonators on Glass.

The results obtained for resonators on glass are shown by curves in Figs. 8, 9 and 10. For the most part sheet glass 3 mm. thick was used. For the transmission work the check system for getting $M' / C'$ was often a second plate of sheet glass bare of resonators, but as this was compared with air or empty frames the ordinates represent the actual percentages of reflection or transmission. The functions of the two glass plates were often interchanged. To facilitate the process of cutting down the resonators coördinate paper

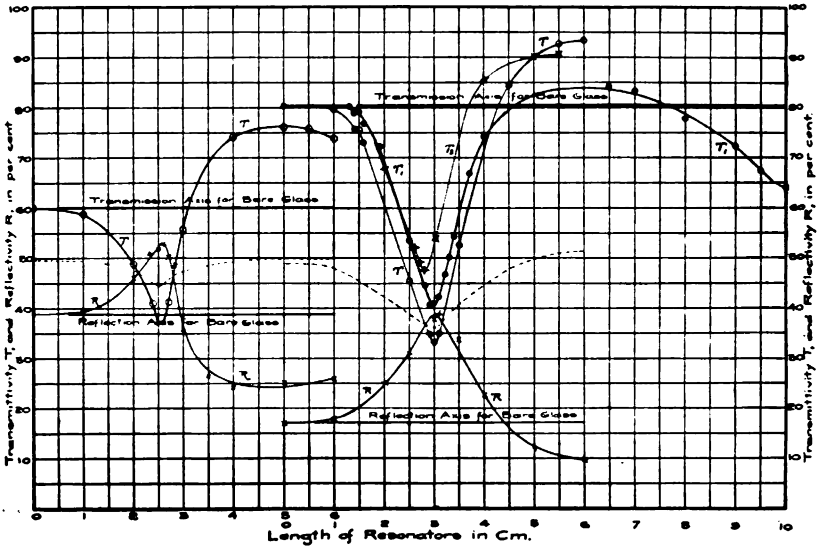

Fig. 9. Fig. 8.

was pasted on the backs of both plates, after the method of Aschkinass and Schaefer. When bare they agreed quite well with each other and with themselves from day to day, never deviating more than 2 per cent. of the incident energy from the mean, viz., 80 per cent. transmission and 17 per cent. reflection.

A study of curves $T$ and $T_1$ in Fig. 8 in connection with the table shows that within the limits there specified a change in the end-on distance between resonators does not affect the resonance-length, which was 3 cm. in both curves. An attempt was made in both of these curves to locate the first upper partial of the vibrator. Though weak it was detected, as shown for the length 1.5 cm. It was found impossible to locate any upper partials beyond the first for if present they were too feeble to admit of measurement.

Perhaps the most interesting feature of the curves in Fig. 8 is that they all cut the axes for bare glass. This means that for strips on glass 3 cm. apart and of length about twice the resonating length the system transmits more and reflects less energy than for the glass plate bare. We shall refer to this phenomenon as that of *extra transmission.* It will be discussed later. It is seen that it is a maximum in this case for a length twice the resonance-length ; and as shown by $T$ it is a rather large effect, being 13 per cent. for this 13-column distribution.

The dotted curve shows, as in Fig. 6, increased scattering at the resonance-length. This result was obtained in every case where the trouble was taken to secure both the $T$ and corresponding $R$ curves.

As is usual with sheet glass the pieces used were slightly warped and so to make sure that none of the effects obtained were due to lack of planeness, especially because of the finite dimensions ($12 \times 10\lambda$) of the glass, one set of curves was taken using plate glass (6 mm. thick). They are shown as curves in Fig. 9, and it is seen that the type is the same as before. The distribution was the same as for Fig. 8, $T$ except that the end-on distance at the start was 1.0 cm. instead of 0.5 cm. The *extra transmission* is slightly greater than before, about 16 per cent. It is seen, too, that the reflection from the thicker glass is greater and the resonance-length less (2.55 cm. instead of 3 cm.) than for the sheet glass. For resonators this same distance of 3 cm. apart in air the resonating-length was 5.3 cm. It is doubtful if, following Aschkinass and Schaefer, the index of refraction of the glass could be obtained from these figures, for the thickness of the glass as well as the fact that it is on only one side of the resonators serves to make the relation a complicated one.

A comparative study of the curves in Figs. 8 and 10 with reference to the table of distributions shows that a variation in the side-on distance between strips materially alters the resonance-length and in a manner similar to the case of resonators in air.

The most typical resonance curve is $T_1$, Fig. 8, for which the strips were 3 cm. apart. When 5 cm. apart the effect is smaller, as shown in $T_2$, and for 4 cm. distance the curve (not shown) lies in value between $T_2$ and $T$.

For distances apart smaller than 3 cm. (see Fig. 10) the absorption keeps increasing in amount with diminishing distance, but the sharpness of the resonance continually grows less until for a 1 cm. distance the exact location of the absorption maximum is indefinite, so flat has the curve ($T$) become. It was estimated at 5.2 cm., but it may easily be 2 or 3 mm. more or less than this. Thus we may say that for resonators on glass the absorption-maximum practically disappears when they are $\frac{1}{10}$ of a wave-length apart. The same thing seems probable for resonators in air.

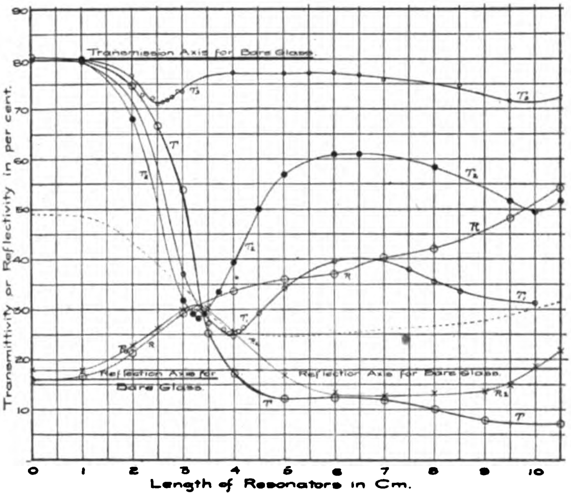

Fig. 10.

The dotted curve in Fig. 10 is the mean of $R$ and $T$ and shows how great the scattering becomes when the resonators are close enough together to interfere strongly with one another. The mean of $R_2$ and $T_2$ is not shown, but the fact that $R_2$ cuts the reflection axis for the bare glass plate while $T_2$ does not cut the transmission axis shows the magnitude of the scattered energy. For zero length $R$ and $R_2$ differ by 2 per cent. of the incident energy, due to lack of planeness of the glass and to experimental error.

In all of the work on reflection the resonator face of the glass plate was toward the vibrator, but in the transmission work it was found immaterial which surface faced the vibrator. For instance, $T_2$, Fig. 8, was taken with the resonator surface of the glass toward the vibrator while $T$ was taken with it in the opposite position. In fact, to test the idea, when the resonance length of $T$ was reached the plate was purposely turned 180° ; there was no alteration in the transmitted energy.

As was found for the case of the main receiver (Fig. 2) one would expect for the resonators a second absorption-maximum at a length three times the fundamental length, and indeed this second maximum appears in its proper position in $T_2$, Fig. 10. But $R_2$ does not support $T_2$ in this respect and in $T_1$, Fig. 8, it is displaced 1 cm. to the right. The displacement of this second maximum is shown most strongly in $T_3$, Fig. 10, taken for a set of resonators 10 cm. apart. It would seem that for causes difficult to explain, the location of this second maximum for any given case cannot be successfully estimated ; to be able to predict it the law of scattering would need to be known. It is interesting to notice, however, that in all the curves, no matter what the length of maximum resonance, this second maximum occurs at the length 10 cm. It is difficult to give an unequivocal interpretation of this result, but it should be noted that at the beginning of any seven-column distribution curve the end-on distance between resonators was small (though in no case less than 5 mm.) and for such distances capacity effects due to charges on the ends of the strips might be felt. This is not borne out, however, by curve $A$ Fig. 11 (see below), for if the charges on the ends of the strips exert an appreciable influence for end-on distances as small as 5 mm. the first point on this curve should not be on the straight line the curve shows.

Although the relation between the first and second absorption-maxima is not clear from the experiments, still the first absorption minimum always (including the case of resonators in air) occurred at the length twice the fundamental length, provided the strips were not closer together than 2 cm. Now Rubens and Nichols,[1] working with heat-waves 24 $\mu$ long reflected from fluorite, measured the reflection from silver resonators on glass for a number of different lengths varying by successive steps of 6 $\mu$ and found maxima of reflection for the lengths 12 $\mu$ and 24 $\mu$ and a minimum at 18 $\mu$. In other words, they obtained reflection maxima for resonators whose length was a whole number of half wave-lengths, whereas we find such maxima only for odd multiples of the half wave-length. The form and distribution of the resonators on glass studied by Rubens and Nichols were so different from any case examined in the present paper that no strict comparison between their results and the present ones is possible. One assumption used in the interpretation of their results, namely, that the resonators and the glass background reflect separately and independently, seems from the present results very doubtful.

Curve *G* in Fig. 7, summarized from Figs. 8 and 10, expresses the relation between the side-on distance between strips and the resonance length. It becomes a straight line for distances greater than 4 cm., and though it slopes less than *A* does, it still makes an appreciable angle with the axis of abscissas. Had points on *A* been obtained for distances under 3 cm. the curve would show in all probability the relatively sharp bending that *G* does for such distances.

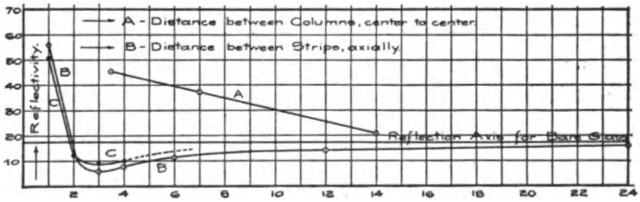

Fig. 11.

Starting with a dense distribution of columns of strips of the resonating-length it was thought interesting to measure the reflection as alternate columns were removed. Accordingly measurements were taken of a 27-column set of resonators 3 cm. long, 3 cm. apart sidewise and 0.5 cm. apart end-on, then for a 13-column set and finally for seven columns, care being taken, of course, always to leave the central column. Using as abscissas the distance between the axes of adjoining columns the curve (*A*, Fig. 11) plots a straight line.

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[1] Rubens and Nichols, PHYS. REV., Vol. V., p. 152, 1897.

## 5. LONG STRIPS ON GLASS.

In the endeavor to get more light on the observed phenomenon of *extra transmission* strips 2 mm. wide and of a length equal to the entire width of the plate were pasted on the glass at intervals of 4 cm. Such a set reflected 8 per cent. and transmitted 92.9 per cent. by measurement, the bare glass reflecting 17.5 per cent. This set being then rendered worthless by further experimentation which did not prove fruitful, another set of long strips 1 cm. apart was prepared. The coefficient of reflection having been obtained alternate strips were then removed and measurements again taken. The fact that the greatest *extra transmission* for a system of double the resonating-length had been obtained when the strips were 3 cm. apart (*T*, Fig. 8) had led us to suspect that 3 cm. was a critical distance, and so for the first removal of strips only every third instead of every other one was left. The results are shown in curve *B*, Fig. 11, while curve *C* shows the corresponding figures, estimated from Figs. 8 and 10 for a system of double the fundamental length. Both the reflection for 1 cm. distance and the *extra transmission* for the other distances are slightly greater for *B* than for *C*. Now curves $R_2$ and $T_2$, Fig. 10, show that while for a 2 cm. distance there is less reflection from the system of double length than from the bare glass plate, still the extra energy is scattered, not transmitted; *T* and *R*, Fig. 8, on the other hand, show that when the distance is 3 cm. the excess is actually transmitted, that the scattering is nothing. Hence it would appear that *extra transmission* occurs for long strips on glass when further apart, say than 2.5 cm. or $\frac{1}{4}\lambda$. We are inclined to think that it occurs for strips on glass any distance apart greater than $\frac{1}{4}\lambda$ and of any length greater than the fundamental length provided the length chosen is not near a secondary absorption-maximum; this idea was only partially tested however.

Perhaps the simplest explanation of the observed phenomenon of *extra transmission* and correspondingly decreased reflection which may be at present tentatively offered, is that the combination of metal strips and glass constitute a medium with a refractive index different from that of glass alone. The optical dispersion formula[1]

$$n_\lambda^2 = b^2 + \sum \frac{M}{\lambda^2 - \lambda_1^2}$$

leads directly to such a result. Thus if for the glass alone $n = b$, then when the plate is covered with resonators of a given length,

$$n_\lambda^2 = b^2 + \frac{M}{\lambda^2 - \lambda_1^2}$$

in which $n_\lambda$ is the index of refraction for the wave-length $\lambda$ of the incident-radiation and $\lambda_1$ is the wave-length corresponding to the natural period of the resonators ; $b^2$ is the dielectric constant of the medium. Hence when $\lambda_1 \gtrless \lambda$ then $n \lessgtr b$. In all cases where *extra transmission* was observed $\lambda_1 > \lambda$ hence $n < b$, which is as it should be to give decreased reflection and a correspondingly increased transmission.

Seen from this point of view, the present case is analogous to that of quartz in the visible spectrum, where $n < b$, hence quartz shows smaller reflection and larger transmission for visible than for the longer electric waves. In both instances the anomalous behavior is due to the presence in the medium of structures which respond to longer waves than those present in the incident radiationl

So far as the present writers are aware this phenomenon of *extra transmission* has not hitherto been noticed for electric waves.

### 6. Long Strips Cut into Resonating-lengths.

The resonating-length having been determined for certain side-on distances between strips both in air and on glass, it was considered of sufficient interest to compare the reflection percentages from long strips entire and when cut into resonating lengths. Strips 77.3 cm. long and 3 cm. apart in air reflected 39.8 per cent. of the incident energy; when these were cut into 13 columns of resonators 5.3 cm. long with a 0.7 cm. end-on distance the reflection was 79.0 per cent., a two-fold increase.

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[1] Drude's Optics (English translation), p. 391.

For the same distance apart on glass *extra transmission* occurred in the case of long strips, and so where strips of great length when entire reflected only 5.6 per cent. of the incident energy, when cut into 27 columns 3 cm. long and 0.5 cm. apart end-on the reflection was 46.0 per cent., an eight-fold increase.

### 7. REFLECTION AND TRANSMISSION OF A WIRE GRID.

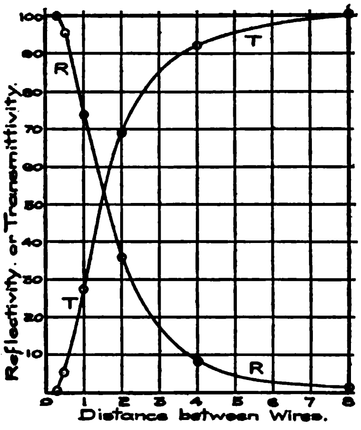

Fig. 12.

For measuring the reflection and transmission of a wire grid fine copper wire (B. &. S. No. 34) was attached to a large (125 × 100 cm.) wooden frame at intervals of 2.5 mm., and measurements were taken as the grid-constant was successively increased by removing alternate wires. The results are shown as curves in Fig. 12. The reflection is seen to be total when the spacing is 2.5 mm. or one fortieth of a wave-length and zero when it is 8 centimeters or four fifths of a wave-length.

### 8. COMPARISON OF WAVE-LENGTH WITH RESONATOR-LENGTH AND WITH RECEIVER-LENGTH.

Using two different separating surfaces the principal wave-length was found to be 9.9 cm. Although in getting the curve in Fig. 2 for the tuning of the receiver no means were provided for taking account of the deterioration of the vibrator the error thus introduced in locating the tuned length of the receiver at 4.0 cm. is of the second order. This is confirmed in the curve, moreover, by the second maximum occurring quite accurately at 12.0 cm. Thus the ratio of wave-length to receiver length is 2.47, confirming MacDonald's[1] value of 2.53 over Poincaré's[2] value of 2.

Curve *A*, Fig. 7, shows that neighboring resonators no longer influence each other in a way to change the length for maximum resonance when a whole wave-length apart sidewise. Beyond this distance the curve becomes a straight line, and the length of maximum resonance in a system so spaced should be the same as that for a single uniform linear resonator. For 10 cm. waves the chief resonance-length was found to be 4.4 cm. and the ratio $\frac{\text{wave-length}}{\text{resonator-length}} = 2.25$, which agrees neither with Poincaré's nor with MacDonald's theoretical value, but is midway between the two values.

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[1] MacDonald, "Electric Waves," p. 111.

[2] Poincaré, "Les Oscillations Electriques."

The experimental evidence for this result is given in curves[1] $T_2$ and $T_3$, Fig. 6. $T_2$ shows the transmission as a function of the resonator length when neighboring resonators were 10 cm. apart sidewise, and $T_3$ shows the same function for resonators 20 cm. apart. The abscissas of the minima in both cases are fairly well marked and cannot be read as low as 4 cm., which would be necessary to establish MacDonald's ratio, nor can they on the other hand, be read as high as the 5 cm. length, required by Poincaré. The only question which can arise therefore is one concerning the accuracy of the wave-length measurement. The writers feel reasonably sure that the wave-length cannot be in error by an amount large enough to bring about even an approximate agreement with either theory.

Willard and Woodman[2] found an agreement with MacDonald's ratio for the resonance length of thermoelectric receivers, and their result is confirmed earlier in the present paper. In the thermoelectric receivers, however, a relatively high resistance occurs at the thermojunction and also a sharp constricting of the current stream lines. Such conditions undoubtedly affect the linear dimensions for maximum resonance, and it is therefore not surprising to find the resonance length for receivers different from that for uniform linear resonators.

## 9. CONCLUSIONS.

As a result of the present study it appears:

1. That for a system of linear resonators, the length for maximum resonance is, within fairly wide limits, independent of the distance apart of resonators in the direction parallel to the electric force, but

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[1] The observations for curves $T_2$, $T_3$ were made for the writers by Messrs. Woodman and Webb after the other experiments embodied in this paper were completed.

[2] Willard and Woodman, l. c.

varies in an inverse manner with the distance between resonators in a direction perpendicular to the electric force.

2. That the mutual influence between resonators at side-on distances greater than a wave-length of the incident radiation ceases to affect the length for maximum resonance appreciably.

3. That the resonator length for maximum resonance depends upon the dielectric properties of the plate to which the resonators are attached.

4. That secondary resonance maxima occur only at odd multiples of the fundamental resonating length.

5. That neither the Hertz-Poincaré nor the MacDonald ratio for the quotient of wave-length by resonator length holds for a uniform linear resonator.

6. That certain systems made up of resonators of lengths differing with the distribution over the surface of a glass plate, transmit more energy than the same glass plate when bare, and that a simple and general explanation of this result is afforded by the theory of optical dispersion.

7. That it is possible to increase the reflection from a grid of very long strips any distance apart by cutting them up into lengths equal to the resonance length for that distance.

8. That the distance apart of fine wires in a grid to be perfectly opaque to electric waves of length $\lambda$ when the wires are parallel to the electric force, should be of the order $\frac{1}{40}\lambda$. When at a distance $\frac{4}{5}\lambda$ apart the same wires transmit practically all of the incident radiation.

In closing we wish to express our indebtedness to Messrs. L. E. Woodman, H. W. Webb, F. A. Thomas and S. R. Williams for their kindly assistance rendered at various times in taking some of the observations. To Professor Hallock we are grateful for kindly interest, encouragement and friendly advice. We are especially indebted to Professor E. F. Nichols, who suggested the problem and some details of the methods for solving it.

PHOENIX PHYSICAL LABORATORIES,
COLUMBIA UNIVERSITY,
February, 1906.

NOTE. — Since the foregoing paper was written the results of an investigation by M. Pietzold, Ann. d. Phys., 19, p. 116, 1906, in some respects similar to the present one, have come to the attention of the writers.

# THE DURATION OF THE AFTERGLOW PRODUCED BY THE ELECTRODELESS RING DISCHARGE.

By C. C. Trowbridge.

## Introduction.

THE phosphorescence which is produced in a gas by the electrodeless ring discharge and known as the afterglow, has been studied chiefly by J. J. Thomson,[1] H. F. Newall,[2] and J. B. B. Burke,[3] who have established a number of facts concerning the phenomenon. The nature of the afterglow, however, has not been explained and the conditions on which it depends have been little understood.

The purpose of the investigation described in the present paper was to determine some of the conditions under which the afterglow is formed by making a series of systematic observations on the duration of the afterglow in air at different pressures and with different conditions of the electrical system.

The duration of the afterglow does not appear to have been systematically studied heretofore and a number of new facts have been determined by this method of investigating the nature of the phenomenon.

The subject is of interest, both on account of its theoretical bearing, and because the afterglow has a suggestive resemblance to certain unexplained glows which occur in the upper regions of the earth's atmosphere, namely, the persistent luminous streaks or trains which are produced by very large meteors. It was in connection with an investigation relating to these meteor trains that a study of the afterglow was made.

The observations on duration of the afterglow have been extended also to very low temperatures, such as might be expected at great altitudes above the surface of the earth, by subjecting the rarefied gas in which the afterglow was formed to the temperature of liquefied air, and the behavior of the afterglow has been studied when under these conditions. This paper contains the following sections:

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[1] Thomson, Recent Researches, p. 185, 1893.

[2] Newall, Proc. Camb. Phil. Soc., Vol. 9, p. 295, 1897.

[3] Burke, Phil. Mag., 6 s., Vol. 1, p. 342, 1901.

1. Previous investigations on the afterglow.
2. Arrangement of the apparatus.
3. Method of observation.
4. The variation of the duration of the afterglow with change of gas pressure.
5. The change in the duration curves when the electrical intensity of the field in the discharge vessel is varied.
6. Critical gas pressures where the afterglow is not readily formed.
7. The effect on the duration curve of changing the frequency of oscillation of the system.
8. The duration and behavior of the afterglow at liquid air temperatures.
9. Conditions which effect a change in the rate of decay of the afterglow.
10. The spectrum of the afterglow.
11. Points of resemblance between persistent meteor trains and the afterglow.
12. Summary and conclusions.

## 1. PREVIOUS INVESTIGATIONS ON THE AFTERGLOW.

Worrem[1] and Sarasin[2] have given accounts of phosphoresence in rarefied gases produced by electrical discharges and both have agreed that it does not occur in the case of a pure simple gas.

The afterglow formed by the electrodeless ring discharge was first investigated by J. J. Thomson,[3] who found that the gases which show the afterglow are those which also readily form polymeric modifications, and that in the case of oxygen the glow seems to come from ozone and the phosphorescence to be due to the gradual reconversion of the ozone into oxygen.

In a paper on "Luminosity Attending the Compression of Certain Rarefied Gases," H. F. Newall[4] states that he obtained afterglows of the following colors: silver-gray, yellow, green, old gold, ruddy yellow, and brilliant blue, and that he was led to connect white phosphorescence with mixtures containing oxygen and carbon compounds, and yellow phosphorescence with mixtures containing oxygen and nitrogen, and blue phosphorescence with mixtures containing oxygen and sulphur.

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[1] Worrem, Pogg. Am., Vol. 126, p. 643.

[2] Sarasin, Pogg. Am., Vol. 140, p. 425, 1870.

[3] Thomson, l. c. Conduct. of Electricity through Gases, p. 498, 1903.

[4] Newall, l. c.

Newall found the spectrum of the afterglow to be continuous. He also observed the interesting phenomenon that when the gas in the apparatus was compressed in the ordinary process of pumping, a glow appeared. This glow was obtained only in the pump bulb and after an electrical discharge had taken place in the receptacle used for that purpose, which was connected to the pump bulb by a small bore tube six or eight feet long. The pressures at which he obtained the pressure glows were between 0.5 and 0.3 mm.

J. J. B. Burke[1] has also published a paper "On the Phosphorescent Glow in Gases." He found that when wire gauzes were placed at points along a tube through which the afterglow was diffusing, and these gauzes attached to the terminals of a small Wimherst machine in action, the afterglow appeared "to travel down the tube with undiminished intensity and velocity," and that when an electromotive force from 180 storage cells was substituted for that from the Wimherst, the result was the same. This is evidence that the glow does not accompany recombination of the ions. He showed that a destructive effect was produced on the afterglow by subjecting it to cathode rays, and also found "that the glow conducts as it passes through the gas." This subject was investigated at some length by Burke, but the above results seem to be the most important.

A paper by Percival Lewis[2] on a new phosphorescence phenomenon contains an account of an afterglow in many respects similar to that formed by the electrodeless discharge, especially in regard to its spectrum, to which reference will be made later on.

## 2. Arrangement of the Apparatus.

The method of producing the electrodeless discharge in the writer's experiments was the same as that originally adopted by J. J. Thomson.

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[1] Burke, l. c.

[2] Lewis, Astrophys. Jour., XII., July, 1900.

The inner coatings of two or more Leyden jars, *LL*, Fig. 1, were connected to the spark gap *S* and also to the terminals of a powerful induction coil; the outer coatings of the jars were joined to the helical coil *C* which surrounded the glass vessel in which the discharge was produced. The vessel was connected to a mercury air pump provided with a drying bulb and a McLeod gauge.

The spark gap consisted of two brass balls one centimeter in radius each and their distance apart could be varied by means of a micrometer screw. Whenever a spark passed between the brass balls of the spark gap *S* the rapid alternating current set up in the coil *C* around the glass vessel *V* by the discharge of the jars gave rise to an alternating electromotive force in the gas in the vessel. At low gas pressures the ring discharge appears, which is followed under certain conditions by the afterglow.

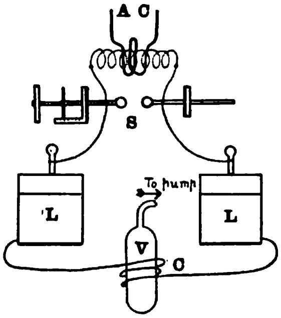

Fig. 1.

The theory of the electrodeless discharge has been worked out by Davis,[1] who used in the course of his experiments both the helical and spiral form of coil, and the only difference between the results obtained was that the discharge is somewhat more easily produced when the helical coil is employed, owing to the static discharge, perpendicular to the plane of the true ring discharge, due to the impedance of the helical coil.

When a large induction coil is employed it is very difficult to keep the balls at the spark gap bright, and therefore it was found best to allow them to become clouded by the discharge in order to assure constant conditions for successive discharges.

It was at first attempted to make the observations by using an induction coil with direct current and a Wehnelt interrupter, but owing to the variations in the action of the interrupter this arrangement was not employed. An unusually powerful induction coil was then procured, and operated by a 60-cycle alternating current. This method proved satisfactory.

The vessel employed at first was a single glass bulb, as shown by

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[1] B. Davis, Phys. Rev., XX., March 3, 1905.

*V* in Fig. 1, which was surrounded by a coil of wire connected with the Leyden jars, but it was necessary to discard this form of vessel because the phosphorescence of the glass produced by the discharge was so bright and persistent as to prevent the moment when invisibility of the afterglow occurred from being noted. In one experiment, after the electrodeless discharge had ceased, the phosphorescence of the glass was observed to remain for *twelve minutes*, air at atmospheric pressure having been let into the vessel immediately after the discharge.

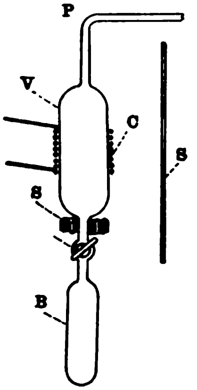

Fig. 2.

The vessel shown in Fig. 2 was finally employed, in which *P* is a tube of about 0.6 cm. bore leading to the pump, etc., *V* a glass vessel 7 cm. in diameter, *B* a small bulb into which the afterglow diffused, *C* a coil of eight turns of insulated copper wire, *SS* screens for cutting off the light from *V* when observing the afterglow in *B*, *SC*, stop-cock, 0.7 cm. bore.

### 3. METHOD OF OBSERVATION.

The method of making the observations of the duration of the glow is explained in detail, because it is generally considered difficult to determine the moment of disappearance of a fading light with accuracy. As seen, however, from the curves in this paper, the various points showing the duration of the afterglow and the corresponding pressure lie within the curves in almost every case.

The duration of the afterglow was taken as the time between the instant of the cessation of the electrodeless discharge and that when the afterglow became invisible; the time being registered by a stop-watch reading to one fifth second.

In order to have constant sensitiveness of the eyes the observations were all made at night and the eyes were always carefully covered by a screen during the time when the electrodeless discharge was taking place. The readings were afterwards recorded by the aid of a dim light. The room and the apparatus were painted black which prevented reflections.

In Table I., four determinations of duration at different pressures of the air are given. These show the agreement of successive readings of the duration of the afterglow in one series of observations. In all the curves given the agreement of the observations is nearly as good. Occasionally apparently abnormal conditions of the gas in the tube were encountered which interfered with the measurements. This matter is considered in the next section (4).

From the figures in Table I. it is evident that the errors from physiological sources are small. This is chiefly owing to the fact that the afterglow is too faint to produce after-images, and that the rates of decrease of intensity of the afterglow in the experiments made were quite rapid except at very low pressures, and thus the moment when invisibility occurred was readily noted at most pressures. The statement concerning the agreement of the readings does not apply, however, to the duration at certain "critical pressures," which are referred to especially in section (6).

At very low gas pressures the variation of the different readings in the same set were larger than at high pressures (as shown by the last column, Table I.), owing to the fact that the rate of decay of the intensity of the glow is slower as the pressure diminishes and the exact moment of invisibility is noted with difficulty.

TABLE I.

*Readings of the duration at different pressure (from Series 12).*

| $p = .28$ mm. Duration in Seconds. | $p = .125$ mm. Duration in Seconds. | $p = .107$ mm. Duration in Seconds. | $p = .020$ mm. Duration in Seconds. |
|---|---|---|---|
| 15.8 | 24.4 | 29.2 | 21.6 |
| 14.2 | 25.4 | 28.6 | 22.4 |
| 14.0 | 24.2 | 31.0 | 23.2 |
| 15.0 | 26.8 | 28.4 | 20.2 |
| 14.6 | 25.4 | 30.4 | 18.8 |
| 14.2 | 27.2 | 30.2 | 25.2 |
| 15.2 | 27.8 | 31.8 | 25.4 |
| 16.0 | 27.4 | 32.4 | 20.0 |
| 15.4 | 25.0 | 30.4 | 24.0 |
| 15.8 | 25.8 | 30.4 | 21.0 |
| 15.2 | 25.9 | 30.28 | 22.2 |

Average variation from the mean at 0.28 mm. pressure 0.62 sec. or 4 per cent.
" " " " " " 0.15 " " 1.08 " " 4 "
" " " " " " 0.107 " " 0.94 " " 3.1 "
" " " " " 0.20 " " 1.86 " " 8.3 "

A series of observations consisted in determining the duration of the afterglow at from ten to fifteen different pressures, beginning at the pressure where the glow was first observed and gradually reducing the pressure by strokes of the pump until a pressure was reached where no afterglow could be obtained, or until it was too faint to be observed accurately. Usually, each determination was the mean of ten readings about one minute apart, and an entire series required from two to three and one half hours About four or five minutes was allowed to elapse each time the pressure of the gas was changed.

### 4. Variation of the Duration With Change of Gas Pressure.

*Agreement of Curves Formed Under the Same Conditions.* — It has been shown in a general way that the duration of the afterglow varied with the pressure, but no measurements have been published. My first attempts to make a continuous curve showing the variation of the duration with change of pressure were unsuccessful, because the first measurements covering a complete curve were not

Table II.

*Spark gap 3 mm. See Fig. 3.*

| Series 1. | | Series 2. | |
|---|---|---|---|
| Pressure in Millimeters. | Duration in Seconds. | Pressure in Millimeters. | Duration in Seconds. |
| 1.90 | 2.4 | — | — |
| 1.11 | 3.4 | — | — |
| 0.80 | 3.9 | 0.72 | 6.08 |
| 0.577 | 5.04 | 0.53 | 5.20 |
| 0.410 | 5.96 | 0.37 | 4.68 |
| 0.30[1] | 3.7 | 0.27[1] | 3.38 |
| 0.224 | 9.58 | 0.22 | 10.5 |
| 0.16 | 22.2 | 0.20 | 13.2 |
| 0.117 | 29.4 | 0.155 | 28.3 |
| 0.083 | 32.8 | 0.112 | 40.5 |
| 0.059 | 31.38 | 0.08 | 42.2 |
| 0.042 | 27.76 | 0.056 | 38.3 |
| 0.030 | 19.2 | 0.040 | 36.8 |
| 0.02 | 10.6 | 0.029 | 27.2 |
| 0.011 | 5.8 | 0.020 | 14.6 |

(Tabulated observations are omitted in all other series, but the results are shown by carefully plotted curves.)

[1] For consideration of durations at these two pressures see section 6.

made in one run, and it was later found that the duration of the afterglow changed if the gas remained in the discharge vessel for several hours even at the same pressure. It has been found that a continuous curve cannot be formed if fresh gas is admitted between observations, but if an uninterrupted run from high to low pressure is made a smooth curve is obtained.

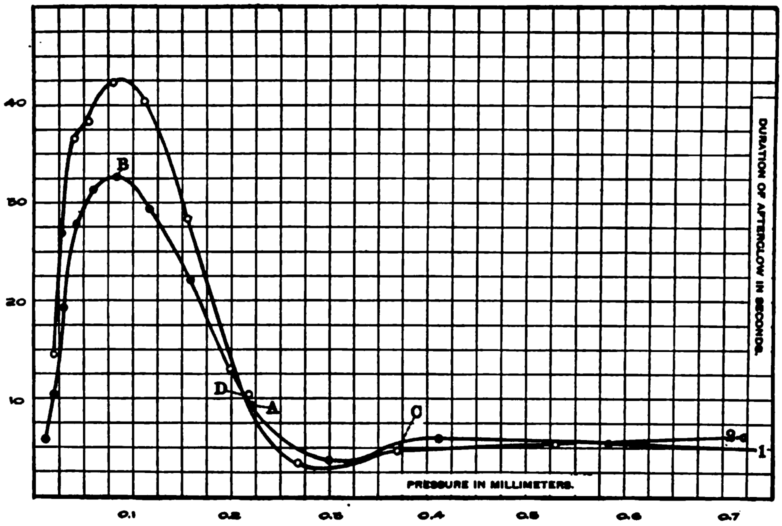

Fig. 3.

Series 1. Spark gap, 3 mm. Volts per cm., 45. Capacity, 6 jars. Period: $9.78 \times 10^{-7}$ sec. Afterglow diffused to lower bulb at A, to drying bulb, etc., at B. Duration at .3 mm., mean of 10 observations, not counting a number of cases where no afterglow appeared.

Series 2. Same electrical conditions as Series 1. Diffusion to lower bulb first noticed at C, bright as afterglow in upper bulb at D, at .27 mm., mean of 24 observations, 3.4 sec. Seven other discharges caused no afterglow.

Series 1 and 2, in Table II., and Fig. 3, were made with the same conditions but several days apart, the difference of duration observed being due to the different states of the gas in the discharge vessel when the experiments were performed. The maximum and minimum points of the curve and the characteristic points of inflection are almost identical, which is the result of keeping the electrical conditions constant. Two other curves are shown in Fig. 7 which were made with a greater sparking potential than series 1 and 2 and hence a higher number of volts per centimeter acting on the gas. These curves were made with the same electrical arrangement and are similar but differ slightly in duration.

In regard to the general form of the curve, the duration in series 1 and 2, Fig. 3, is seen to gradually increase to .4 or .5 mm. pressure, then to decrease to a critical pressure where the afterglow is not always formed, then rise rapidly to a maximum at approximately .8 mm. and then fell to zero. In Fig. 4 three curves are given showing the duration of afterglows formed above .5 mm., the highest pressure at which the afterglow was obtained by me was 2.4 mm.

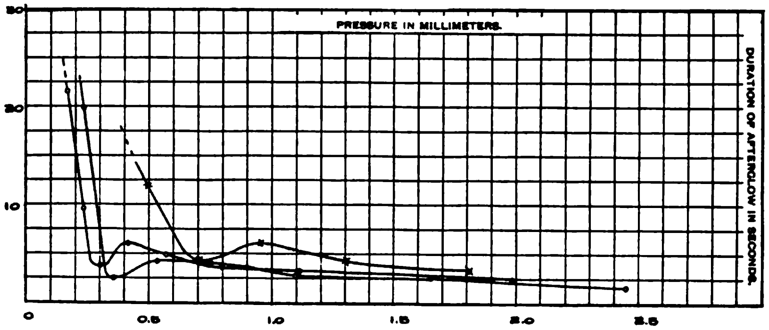

Fig. 4.

Curves showing the relation of the duration of the afterglow to the pressure at pressures greater than 0.5 mm.

*The Effect on these Curves Produced by Changes in the Gas.* — In section 9 the causes bringing about the change of the rate of decay are considered. The changes are such that they unquestionably affect the duration curves. In one experiment it was found that the duration was lengthened 300 per cent. by ten successive discharges, and in others in one hour the duration increased 100 per cent. with no discharges passing during the period. However, in all the observations shown in this paper by curves the successive readings at one pressure were nearly constant as shown in Table I. The effect of an increase of the duration due to a gradual change of the gas in time could not have been more than 10 per cent. Such an effect would tend to displace the curve upward as the pressure is reduced. Moreover, the general shape of the curve, the points of inflection and the effect of changes of electrical conditions are clearly defined in the curves and are but little affected by changes arising from the causes referred to above.

## 5. The Change in the Duration Curves when the Electrical Intensity of the Field in the Discharge Vessel is Varied.

If the spark gap in parallel with the capacity is lengthened an increased electrical intensity acting on the gas in the discharge vessel results. The intensity which can be obtained is largely limited by the surface insulation of the apparatus used. This is shown by a curve in Fig. 5 giving the relation of the spark-gap to the electrical intensity acting on the gas in the discharge vessel. A variation from 45 to 85 volts per cm. was obtainable giving a good

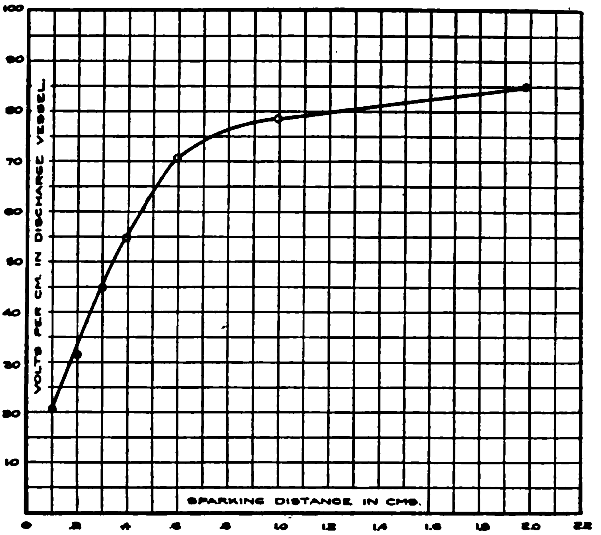

Fig. 5.

afterglow, and a series of observations giving the change of duration with pressure were made through the range as seen in Figs. 6, 7 and 8. Faint afterglows were also obtained at as low as 20 volts per cm. The electrical intensity was measured by means of a coil of wire temporarily replacing the discharge vessel and a micrometer spark-gap in series with this test coil, as shown in Fig. 9 on page 294. The sparking potential was taken from Paschen's tables.[1]

The voltages are slightly greater than those measured owing to a potential perpendicular to the axis of the helical coil; the values in volts per cm., strictly considered, are only relative.

It is seen that the duration curve with 45 volts per cm., series 3, Fig. 6, has a sharp maximum and also a definite minimum. At the latter point the formation of the glow is uncertain. On increasing to 55 volts per cm., series 4, the maximum has begun to disappear and when the volts per cm. are above 70, series 5, 6, 7 and 8, Figs. 7 and 8, the shape of the curve is seen to be completely changed. Therefore, when using high electrical intensities the maximum no longer occurs at pressures which give the greatest intensity but is shifted to the side of lower pressures, since the rate of decay of the afterglow is progressively lessened with diminishing gas pressures.

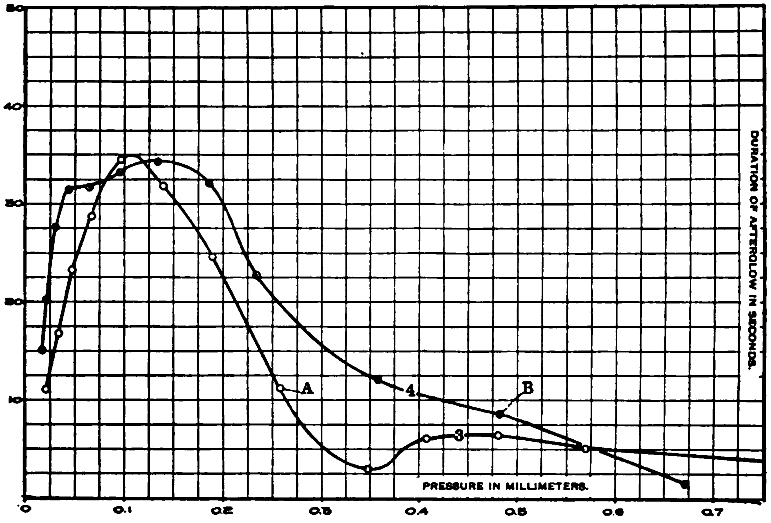

Fig. 6.

Curves Showing the Effect of Changing Electrical Intensity.

Series 3. Spark gap, 3 mm. Volts per cm., 45; larger induction coil than used in Series 1 and 2. Capacity, 2 jars. Period: $5.65 \times 10^{-7}$ sec. Afterglow first readily diffused to lower bulb at A.

Series 4. Spark gap, 4 mm. Volts per cm., 55. Other conditions as in Series 3. First diffusson to lower bulb at B.

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[1] Wied. Ann., 37, 1889.

This effect is partly concealed in the duration curves which do not show the relative initial intensities of the afterglow at different pressures. It is hoped that experiments now in progress on the rate of decay of the afterglow at different gas pressures may make it possible to show this quantitatively.

## 6. CRITICAL GAS PRESSURES WHERE THE AFTERGLOW IS NOT READILY FORMED.

In the ordinary process of forming a curve showing the change of duration with the change of pressure, a critical pressure was usually encountered where the afterglow was not always formed. In different experiments this pressure varied from .29 mm to .75 mm. according to the spark gap used. For all pressures in both directions from the critical pressure, except under certain apparently abnormal conditions, the duration of the afterglow was approximately constant for successive discharges, and followed every discharge when the afterglow once appeared.

Several typical cases will serve as illustrations: In series 1, Fig. 3, the duration of the afterglow was of 2.4 seconds at 1.9 mm. pressure. It then increased steadily to 5.8 seconds at a pressure of 0.4 mm. At the next stroke of the pump, bringing the pressure to 0.3 mm., the critical point was encountered. Here the mean of ten observations gave only 3.7 seconds duration, not including a number of discharges which produced no afterglow. In series 2 an afterglow of 6.1 seconds duration decreased steadily until at .27 mm. the mean of 24 observations was only 3.4 seconds, 7 discharges in this run giving no afterglow. The mean of the five longest durations was 5.5 sec. The critical pressure is seen by the curve, Fig. 3, to be approximately .29 mm.

In series 3, Fig. 6, the influence of the critical pressure was found at both .349 mm. and .259 mm. At both pressures there were about the same number of discharges where the afterglow was not formed. The critical pressure from the curve appears to be .35 mm., a different capacity being used in series 3 than in 1 and 2. It has been further observed that this critical pressure is the point at which the white discharge begins. In one set of 39 observations 23 discharges colored white mixed with pink were followed by an afterglow, 3 pink with a little white gave no afterglow, and 13 pink produced no afterglow. Thus the formation of the afterglow at the critical pressure is intimately associated with the beginning of the white discharge. This is a curious fact, since in all the above series the afterglow had already occurred regularly at higher pressure after pink discharges.

It was only at low electrical intensities that the critical pressure was easily studied; with high intensities the afterglow rarely appeared until the gas pressure was reduced to a point at which the white discharge occurred.

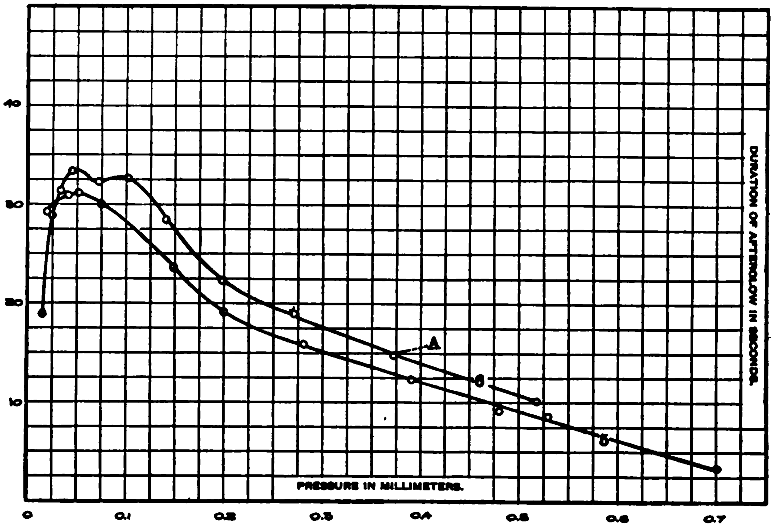

Fig. 7.

Curves Showing the Effect of Changing Electrical Intensity.

Series 5. Spark gap, 6 mm. Volts per cm., 70.8. Other conditions as in Series 3.
Series 6. Spark gap, 6 mm. Volts per cm., 70.8 (duplication of series 5). First observation of afterglow from lower bulb at A.

The experiments thus seem to show that a critical point in the formation of the afterglow coincides with the pressure at which the white discharge begins, and also that the point moves toward higher pressures as the volts per cm. increase, as shown by Table III. In every case in this table except two, the afterglow had already appeared before the critical pressure was reached, and the duration at the critical pressure was less than previously obtained at higher pressure.

The variation in the critical pressure above 60 volts per cm. shows that the uncertain point extends over a greater range of pressure as the spark gap is increased. This may be due in part to the uncertain action of the spark gap.

TABLE III.

| Intensity V. per cm. (Approx.). | Duration of Afterglow, Seconds. | Critical Pressure mm.[1] | Remarks. |
|---|---|---|---|
| 45 | 3.7 | 0.30 | 10 observations; other discharges producing no afterglow not considered in mean. |
| 45 | 3.4 | 0.27 | 24 observations and 7 misses critical pressure as shown by curve, .29 mm. |
| 45 | 3.0 | 0.36–0.26 | Curve shows critical pressure at 0.35 mm. |
| 55 | 12 | 0.36 | 10 observations, 3 misses. |
| 55 | 2.7 | 0.34 | Missed repeatedly. |
| 58 | — | 0.46 | Only a few afterglows obtained. |
| 71 | 5.0 | 0.54 | Only a few afterglows. |
| 71 | 3 | 0.87 | |
| 71 | 3.4 | 0.70 | Many misses. |
| 71 | — | 0.75 | " " |
| 78 | 4.1 | 0.75 | 4 misses to 1 afterglow. |
| 80 | 4.1 | 0.69 | Very irregular, no misses, probably below critical pressure. |

[1] Approximate only, being the nearest gas pressure readings to the critical points on the curves.

## 7. THE EFFECT ON THE DURATION CURVE OF CHANGING THE FREQUENCY OF OSCILLATION OF THE SYSTEM.

The effect on the formation of the afterglow produced by employing different capacities in the system was determined, and it was found that the entire duration curve was slightly shifted by changing the capacity. The effect is due to the change in the frequency of oscillations, since the periodic time, $T$ is equal to $2\pi\sqrt{LC}$, in which $C$ is the capacity and $L$ the self-induction of the system.

At the suggestion of Dr. Bergen Davis the same Leyden jars were used as were employed by him in his experiments on the electrodeless discharge, in order to determine if the maximum of the duration curve occurred at the same pressure as the minimum sparking potential, and if its position changed when the frequency of oscillation was varied. It was necessary to employ not only the same capacities, but also a coil having the same self-induction as in his experiments in order to obtain the same frequency ; therefore the two inductances were carefully balanced on a double-wire Wheatstone bridge. The capacities employed were as follows :

Two jars, arranged as in Fig. 1, $C_1 = 1.6 \times 10^{-18}$.

Four jars, two in parallel, two in series, $C_2 = 3.2 \times 10^{-18}$.

Six jars, three in parallel, two in series, $C_3 = 4.8 \times 10^{-18}$.

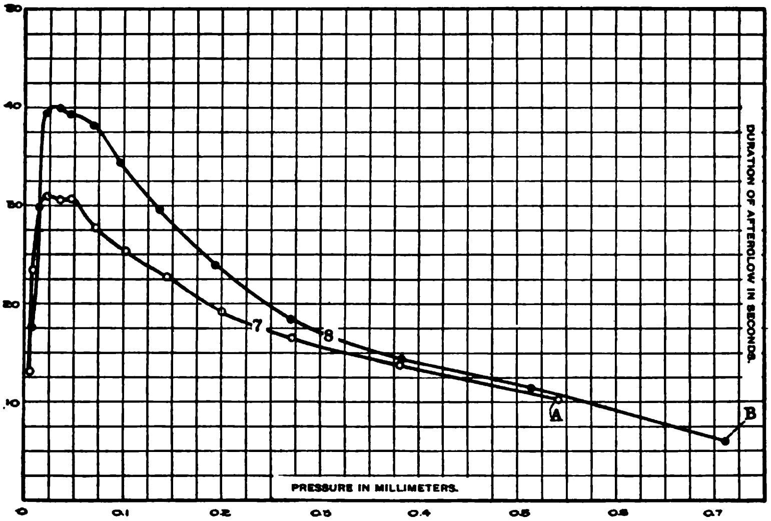

Fig. 8.

CURVES SHOWING THE EFFECT OF CHANGING ELECTRICAL INTENSITY.

Series 7. Spark gap, 10 mm. Volts per cm., 78.6. Other conditions as in Series 3. First observation of afterglow from lower bulb at A.

Series 8. Spark gap, 20 mm. Volts per cm., 84.8. First observation of afterglow from lower bulb at B.

The frequency of oscillations was changed without altering the ratio of the intensity acting on the gas to the potential at the spark gap, by making the above changes in capacity. The periodic time calculated from the formula $T = 2\pi\sqrt{LC}$, in which $L = 5.064$ cm. was as follows :

2 jars, $T_1 = 5.65 \times 10^{-7}$ sec. 4 jars, $T_2 = 7.87 \times 10^{-7}$ sec.

6 jars, $T_3 = 9.78 \times 10^{-7}$ sec.

It was not only found that the duration curve was shifted by changing the frequency of oscillation, but that the pressure giving the maximum duration of the afterglow when using low electrical intensities corresponded to the pressure at which the electrodeless discharge is most easily started, or where the minimum sparking potential for air occurs as determined by Dr. Davis.

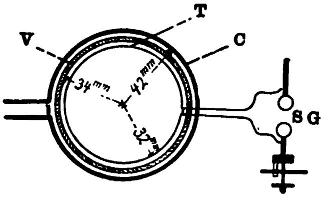

Fig. 9.

V, glass vessel; C, large coil; T, small test coil; S G, micrometer spark gap. Electrical intensity measured 2 mm. from inside of glass vessel.

It is only in the case of the afterglow produced by low electrical intensities that the coincidences occur, since it is only at such intensities, less than 50 volts per cm., that the gas pressure for maximum of luminosity of the afterglow more nearly corresponds to the pressure for maximum of duration.

The following table shows the gas pressures of the minimum sparking potential and the maximum of duration with the various frequencies used.

Table IV.

| Capacity. | Periodic Time Seconds. | Minimum Sparking Potential Pressure. | Maximum of Duration of Afterglow Pressure. |
|---|---|---|---|
| 2 jars | $T_1 = 5.65 \times 10^{-7}$ | .070 mm. | .08 mm. |
| 4 jars | $T_2 = 7.87 \times 10^{-}$ | —— | .091 |
| 6 jars | $T_3 = 9.78 \times 10^{-7}$ | .096 | .10 |

The exact pressure at which the sparking potential is a minimum is somewhat difficult to measure, but, considering the nature of the curves shown by dotted lines in Fig. 10, the agreement is fairly good.

According to Dr. Davis' experiments[1] the pressure at which the minimum sparking potential occurs for a certain period of oscillation ($T_1$) is .07 mm. for carbondioxide, .20 mm. for hydrogen and .25 mm. for helium, therefore it is probable that with similar electrical conditions the afterglows if they occur in the case of all these gases would have a maximum of duration at these pressures. The afterglow was found to occur in the case of helium by Davis.

The determination of the maximum of duration of the afterglow appears to be a simple and apparently accurate method of determining the pressure of the gas at which the discharge is most easily started, and when this pressure is found the spark gap can be readily varied and the minimum sparking potential of the gas determined.

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[1] Davis, l. c.

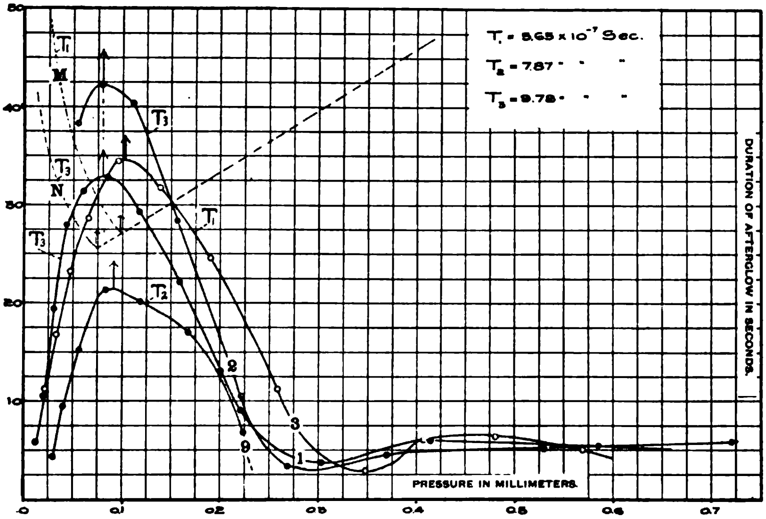

Fig. 10.

Series 1. Spark gap, 3 mm. (45 volts per cm.). Capacity, 6 jars. Periodic time, ($T_3$) 9.78 × $10^{-7}$ sec. Induction coil with A.C.

Series 2. Spark gap, 3 mm. Capacity, 6 jars. Periodic time, ($T_3$) 9.78 × 10.

Series 3. Spark gap, 3 mm. Capacity, 2 jars. Periodic time, ($T_1$) 5.65 × $10^{-7}$ sec. Larger induction coil than used in Series 1 and 2.

Series 9. Spark gap, 3 mm. 4 jars. Periodic time, ($T_2$) 7.87 × $10^{-7}$ sec. Same induction coil as Series 1 and 2.

Curves N and M, minimum sparking potential curves for air with $T_3$ and $T_1$ period of oscillations respectively. (Davis.) The vertical coördinate was intensity, the minimum value being 21.6 volts per cm. for N and 20.4 for M.

## 8. The Duration and Behavior of the Afterglow at Liquid Air Temperatures.

The afterglow was formed at liquid air temperatures in the following manner: The discharge vessel with the surrounding coil was placed within a cylindrical Dewar bulb, as shown in Fig. 11, and an attempt was made to form a duration curve of the afterglow when the vessel had remained for a considerable time immersed in liquid air. The afterglow was obtained at only a few pressures, as shown in Table V., and was then faint and short of duration. With approximately the same conditions a comparison curve at 20° C. was made, which is shown by series 11, Fig. 13. The frost on the Dewar vessel and phosphorescence of the glass made the observations difficult.

Table V.

| Pressure in mm. | Duration (at —186° C.) in seconds. | Pressure in mm. | Duration (at —186° C.) in seconds. |
|---|---|---|---|
| 0.64 | 0 | 0.119 | 8.5 |
| 0.43 | 0 | 0.083 | 21.7 |
| 0.28 | Slight glow | 0.041 | Slight glow |
| 0.19 | Slightly stronger glow | | |

The afterglow, therefore, appeared to be difficult to form at liquid air temperatures, which may be a direct result of a less powerful electrodeless discharge under these conditions. The apparatus was changed to the form as shown by Fig. 12, to determine if the afterglow when formed at normal temperatures would remain bright when it had diffused into a vessel cooled by liquid air. The protecting case about the Dewar vessel was designed to prevent frost from forming and obscuring the glow.

Two curves were made with as near as possible identical conditions. The first, series 12, Fig. 13, was at normal temperatures. The second, series 13, when the glow appeared in a vessel which had been cooled to approximately — 186° C. The observations were not begun until the McLeod gauge indicated the reduction of temperature in the cooled vessel was complete. The vessel was kept surrounded by liquid air for two hours.

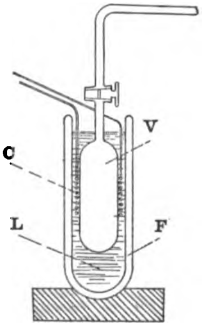

Fig. 11.

V, discharge vessel; C, coil, F, Dewar bulb, L, liquid air.

The important facts revealed are that the afterglow appears bright and of long duration at — 186° C. when it is formed at a normal temperature and allowed to diffuse into the cold vessel; that the resultant curve is displaced considerably to higher pressure, in the present case from .08 mm. to .14 mm. pressure, and also that at every pressure from that corresponding to the maximum of duration to lowest pressure, the afterglow at — 186° C. was much brighter than that in the discharge vessel, although of shorter duration. A comparison at each pressure of the duration of series 12 and 13 is scarcely possible, owing to the fact that the state of the gas was probably different in the two observations. Both series 12 and 13 were formed when the stop-cock connecting the upper and lower vessels (Fig. 12) was open. This permitted the afterglow to continually diffuse into the lower vessel. A series was later obtained in which the large stop-cock shown in Fig. 12 was closed after the discharge as soon as the afterglow had diffused into the lower vessel. A certain body of glowing gas was thus cut off at the temperature of liquid air. The curve obtained, series 14, is seen to be totally different from that of series 13 or when the stop-cock remained open, showing that when the glowing air is confined in liquid air the duration is much shorter than at normal temperatures. The afterglow also becomes less intense than that in the discharge vessel, therefore the shorter duration produced by the low temperature immediately on the closing of the stop-cock does not mean a more rapid discharge of energy.

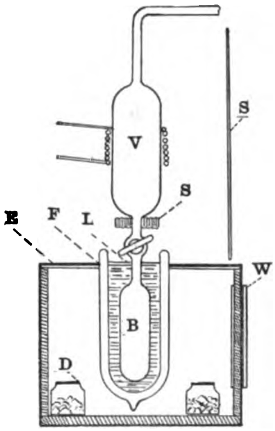

Fig. 12.

V, discharge vessel; B, small bulb; S S, screens, E, enclosure; W, glass window, D, drying material; F, Dewar bulb; L, liquid air.

The afterglow in the discharge vessel during the observations in series 14 increased from about 35 seconds to a maximum of several minutes (series 16). The exact curve was not obtained but a similar curve at about 20° C., shown by series 15 in Fig. 14, was made with the same electrical conditions.

A curious fact of these experiments was that when the afterglow surrounded by liquid air had disappeared, the stop-cock was opened a second time for a moment and then closed, the afterglow diffused into the bulb the second time lasted fully twice as long as when it diffused immediately after the discharge took place. Therefore the duration at — 186° C. in series 14, depended on how soon it was cut off from the discharge vessel. The gradual rising of the duration to a maximum, as shown by series 14, Fig. 14, was probably partly affected by the increase of the rapidity of the diffusion as the pressure was reduced.

The most important fact that is shown by these last experiments (series 14), is that the afterglow can occur in the rarefied gas entirely isolated and surrounded by liquid air.

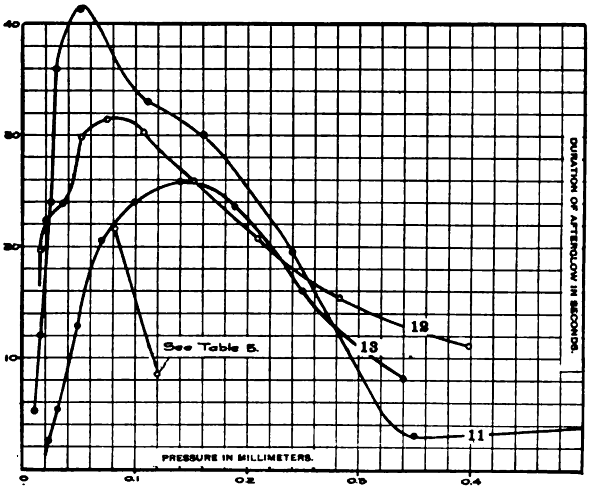

Fig. 13.

Series 11. Formed at 20° C. to show comparison with few observations of afterglow obtained at —186° C. See Table V.

Series 12. Formed at 20° C. for comparison with Series 13. 6 mm. spark gap, 6 jars.

Series 13. In bulb surrounded by liquid air, stop-cock open. Spark gap, 6 mm, 6 jars. Below .1 mm. pressure, afterglow brighter than glow in discharge vessel.

## 9. CONDITIONS WHICH EFFECT A CHANGE IN THE RATE OF DECAY OF THE AFTERGLOW.

The rate of decay of the intensity of the afterglow has not been measured but the duration of the phosphorescence has been observed to become lengthened under the following conditions:

1. *By Repeated Discharges in the Gas.* — The duration of the afterglow is increased under certain conditions by frequent sparking but the increase is noted chiefly when the gas is freshly admitted to the pump and when a number of discharges are passed through

it. Curves have been drawn showing a regular increase of duration from 20 seconds to several minutes. After a number of discharges the duration usually becomes constant.

2. *By Reducing the Pressure of the Gas.* — It has been demonstrated by experiment that increase of pressure of the gas after the afterglow is formed causes a shortening of the duration and a corresponding brightening of the afterglow, and that a reduction of pressure produces a lengthening of duration of the afterglow. This discharge of energy in the gas in the form of a glow by increasing the pressure seems to be similar to the pressure glows obtained by Newall, but in his experiments the pressure glows were only obtained in the pump bulb.

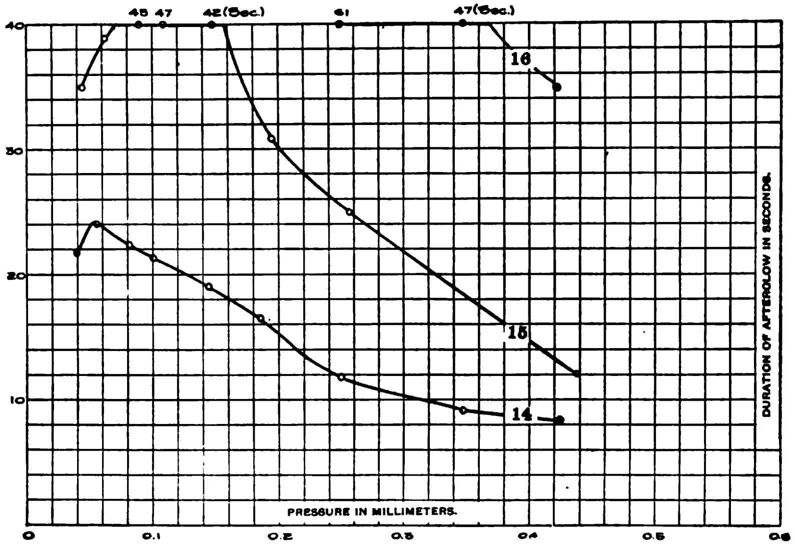

Fig. 14.

Series 14. Formed in the same manner as Series 13, except stop-cock closed after about one second. Bulb surrounded by liquid air. Spark gap, 6 mm. Capacity not determined, 2 large jars.

Series 15. Afterglow in discharge vessel formed at 20° C. for comparison with Series 14.

Series 16. The afterglow in discharge vessel corresponding to readings of afterglow of Series 15. Durations were too long to take entire curve.

3. *By Permitting the Gas to Remain for Some Time in the Discharge Vessel.* — If the gas remains in the discharge vessel and

pump the duration becomes gradually longer. The initial intensity of the afterglow apparently remains the same. This diminution in the rate of decay of intensity occurs whether the air is isolated in a small vessel or connected with the pump and drying tubes. In one case after three weeks the glow increased from 45 seconds to 14½ minutes. The stop-cock leading to the pump was then closed and after three months an afterglow in the same air could be obtained which remained dimly visible for 19 minutes.

4. *By the Reduction of the Water Vapor in the Gas by Drying Materials.* — It has not yet been possible to determine to what extent the pressure of water vapor affects the duration of the afterglow, but it has been found that if the air laden with moisture is admitted to the pump the afterglows then obtained appear more reddish yellow and of short duration, so it is permissible to include water vapor as a fourth condition affecting the rate of decay of the glow. The amount of moisture present is rapidly reduced by the drying material present; but the change of rate of decay of intensity of the glow then depends on at least three conditions and it is difficult to determine to what extent each contributes to this change. The increase in the intensity of a red band in the spectrum of the afterglow occurs when water vapor is allowed to pass into the gas.

## 10. The Spectrum of the Afterglow.

The visual spectrum of the afterglow was observed carefully with a direct vision spectroscope having a scale electrically illuminated, and is given here more as a statement of the general character of the spectrum than the results of a precise spectroscopic study. Such an investigation will require a photographic method. The observations show the visual spectrum to be composed of four prominent and several faint narrow bands, two of which seem to have a line structure, as follows:

6200 — 6160; (approx.) band (see below).
* 5770 — 5730; band, more intense in the middle.
* 5460 ± 5; has the appearance of a clearly cut line. This line also occurs in the electrodeless discharge.
* 5400 — 5350, not as bright as 5460.

5100 — 5050; (approx.) very faint band.
*4345 ± 5; very narrow band or a line; coincident with a corresponding line in the electrodeless discharge.

The bands and lines usually disappear in the following order; (1) (5100 — 5050), (2) (6200 — 6160), (3) (4345), (4) (5770 — 5730, 5460, 5400 — 5350), those starred being the most prominent at first.

The red band (6200–6160) is due to the presence of water vapor. After leaving the air in the apparatus for several weeks with drying material this band entirely disappeared, but on letting water vapor into the pump, etc., the band became nearly as bright as any of the other lines or bands, and when present decayed rapidly as shown above. The nearest correspondence to the red band is the diffuse maxima at 6170 of the oxygen spectrum.[1]

Two lines of the afterglow spectrum bear a close correspondence to two of the mercury spectrum. These lines are 5460 and 4348,[1] and are accounted for by the mercury vapor from the pump. The spectra of the Cooper-Hewitt lamp and the mercury glow in an incandescent lamp bulb both give bright lines which appear to be nearly coincident with those in the afterglow, namely, 5460 and 4340. The spectrum of the afterglow therefore seems to be a line spectrum of mercury combined with a band spectrum.

A yellow afterglow in nitrogen, formed in an *electrode* discharge tube, observed by Percival Lewis[2] showed a band spectrum. The wave-lengths of the centers of the bands were as follows: 6240, 5780, 5740, 5410. These bands show a close correspondence to those in the spectrum of the afterglow formed by the electrodeless discharge.

These observations do not agree with those of Newall,[3] who in a careful and long-continued spectroscopic investigation found the spectrum of the afterglow to be continuous, and only corroborates in part the statement of J. J. Thomson,[4] who records the spectrum in oxygen as continuous, and in air a faint continuous spectrum with a few bright lines. Davis[5] has observed three bright lines as the spectrum of the afterglow in helium excited by the electrodeless discharge. Newall observed the continuous spectrum a very short time after the discharge by means of apparatus which automatically cut off the discharge and exposed the afterglow. He states, however, that the spectrum of the pressure glows observed by him and described in section 1, was composed of four bands. In the writer's observations the spectrum was observed from a half second to a half minute after the discharge, and no change in its character appeared during that time. It seems evident that the spectrum of the afterglow in oxygen is continuous and that in air composed of a number of bright lines and bands, possibly combined with a faint continuous spectrum. Under certain conditions the lines 5460 and 4345 of the afterglow became exceedingly faint as compared to the rest of the spectrum, therefore considerable variation must be expected in the relative intensities of the lines and bands with different experimental conditions.

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[1] Atlas of emission spectra, Hagenbeck and Konen.

[2] Lewis, l. c.

[3] Newall, l. c.

[4] J. J. Thomson, Phil. Mag., 32, p. 335, 1891.

[5] Davis, l. c.

## 11. Points of Resemblance Between Persistent Meteor Trains and the Afterglow.

In the first part of this paper reference is made to the phenomena known as persistent meteor trains, and to the fact that a study of the afterglow was undertaken partly in order to ascertain if there were any points in common between these trains and the afterglow.

Meteor trains are masses of meteoric smoke left in the track of meteors and are self-luminous, sometimes glowing for over thirty minutes. The luminosity appears to be electrical in origin. The height at which the trains occur is between 50 and 65 miles from the surface of the earth. The afterglow bears a strong resemblence to them in a number of respects, and while no conclusion can be reached at this stage of the investigation, enough facts have been found to stimulate further inquiry. Only a short reference to the subject of meteor trains is possible here and a very brief summary of some of the points of resemblance between the two phenomena is as follows:

1. The motion of the meteor through the atmosphere produces an exceedingly high temperature and may bring about chemical or physical changes in the composition of the atmosphere in the track

of the meteor which on reverting to its original state gives out a phosphorescent glow, or the surrounding air may be highly ionized by the vaporizing meteor so that electrical discharges take place great enough to produce an afterglow like that following the electrodeless discharge.

2. The meteor train as well as the afterglow appears to be produced between definite gas pressures; in the former case the atmospheric pressures corresponding to the altitudes 50 and 65 miles, in the latter the air pressure in the discharge tube between 0.5 and 0.05 mm.

3. The rate of diffusion of the afterglow at certain pressures is of the same order as the outward diffusion of the glowing particles of the meteor train, or at the rate of several hundred feet per minute.

4. The spectrum of both appear to be composed of a few lines or narrow bands, but no observations of sufficient accuracy have been made on the spectra of meteor trains to make a more direct comparison possible.

5. Under certain conditions the afterglow dies out first where it is formed, and observations have shown that many meteor trains fade first in the center, or directly in the meteor's track where the train originates.

6. Absence of moisture seems to accompany long duration in the case of the afterglow, and at great altitudes the air must be very dry; thus if the meteor train is an afterglow the long duration of the phosphorescence may be partly accounted for by the absence of moisture.

7. The afterglow can occur in air cooled to —186° C. The glow from the meteor train proceeds from a mixture of gas and extremely fine meteoric dust at the very low night temperature which exists at 50 or 60 miles above the earth's surface. Recently as low as —79.5°C. has been registered at approximately nine miles altitude by a baloon liberated at St. Louis by Rotch.[1] The observation was made at night in January.

A number of the above facts concerning meteor trains have been determined by the writer in a systematic study of the observations of this phenomenon made by different astronomers since 1860. A paper devoted to the subject will appear elsewhere.

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[1] A. L. Rotch, Proc. Am. Acad. Arts and Sci., December, 1905, p. 350.

## 12. SUMMARY AND CONCLUSIONS.

A summary of the facts shown by the present experiments on the duration of the afterglow is as follows:

1. The visible duration of the afterglow can be measured with considerable precision if the eyes of the observer have been previously protected from the strong light so as to insure constant sensitiveness of the retina, and provided the fading of the afterglow is not too slow. Under these conditions errors from physiological causes affecting the measurements are negligible.

2. The electrical system remaining the same, similar duration curves showing the change of duration with change of pressure can be formed giving the same characteristic points of inflection, maxima and minima, but variations in duration in similar curves may occur owing to changes which take place in the gas.

3. The afterglows thus far observed appear over a range from 2.4 mm. to .002 mm. pressure. The range of the glows obtained by Newall being from about 0.6 mm. to .01 mm. only, and the glows observed by Burke being between 0.7 mm. and .02 mm.

4. The maximum of intensity of the afterglow and the maximum of duration are nearly coincident only at low electrical intensities. If the volts per cm. acting on the gas are increased above a certain value the afterglow is formed over a much greater range of pressures, and then the maximum of the duration curve no longer occurs at pressures which give the greatest intensity of luminosity but is shifted to the side of lower pressure, since the rate of decay of the glow is progressively lessened with diminishing gas pressures.

5. There is a critical point on the duration curve where the afterglow is only occasionally formed, and when obtained varies greatly in duration and intensity. This point corresponds closely with the pressure at which the white discharge begins. At this pressure, if the discharge is pink there is no afterglow; if pink intermixed with white then a glow of short duration occurs. The brightest and longest glows appear to follow the whitest discharges. At pressures on both sides of this critical point the time of duration of the glows are nearly constant for successive discharges and glows are obtained after every discharge.

6. The position of the maximum of the curve giving the change

of duration with change of pressure varies with the frequency of oscillation of the discharge, a greater frequency moving the maximum of duration towards higher pressure. With low electrical intensities the pressure giving the maximum duration of the afterglow always corresponds to the pressure where the electrodeless discharge is most easily started, which also varies with the frequency of the oscillation.

7. (*a*) When the electrodeless discharge is made to take place at the temperature of liquid air, the intensity and duration of the afterglow are both greatly diminished, although the glow is formed through a short range of pressures even at this low temperature.

(*b*) When the afterglow formed at 20° C. is made to diffuse into a bulb reduced to liquid air temperature, a passageway being left open to the discharge vessel, the curve of duration is similar to that at 20° C. but the maximum is very much displaced to a higher pressure. The glow is much brighter at pressures below the maximum of duration than it is at normal temperatures but decays more rapidly.

(*c*) If the passageway is closed as soon as the afterglow from a discharge has first diffused into the bulb cooled to liquid air temperatures, the glow is less intense and much shorter in duration than it is at 20° C. formed from the same discharge. Under certain conditions, however, which are not now understood, somewhat similar results are obtained at normal temperatures.

8. The rate of decay of the intensity of the afterglow may be gradually lessened by one or more of the following conditions: (1) A succession of discharges (in certain cases only), (2) change of the gas with time, (3) diminution of pressure while the gas is glowing, (4) gradual reduction of the quantity of water vapor in the gas (independent of 2).

9. While the rate of decay of the afterglow becomes less as the pressure of the gas is reduced, and the rate of recombination of the ions decreases with diminishing pressure at very low pressures, as shown by Hendren,[1] the glow is nevertheless not due to the recombination of the ions, unless fresh ionization occurs after the cessation of the electrodeless discharge, because in the case of small

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[1] PHYSICAL REVIEW, Vol. XVI., November, 1905.

glass vessels the ions are known to disappear in a fraction of a second at pressures as low as those used in the present experiments.

10. The rapid drift of the glow in the tubes of the pump, etc., has been shown by experiment not to be an explosive effect of the discharge but is due rather to ordinary diffusion of the gas, the rate of diffusion increasing as the pressure is reduced. The visible diffusion of the afterglow begins after the appearance of the white discharge; its rate then increases as the pressure of the gas diminishes.

Since the white discharge begins at different pressures depending on the electrical intensity acting on the gas, it follows that diffusion at the same gas pressure is rapid or slow according as the afterglow is formed by the white or pink discharge. Hence it is possible that we are dealing with two conditions in the gas, with widely different diffusing rates. It is significant that the glass vessel in which the electrodeless discharge takes place first begins to show strong and enduring phosphorescence at the pressure at which white discharge appears. This shows a sudden increase in the electronic bombardment of the glass after the white discharge begins.

Further experimentation will be necessary in order to determine the nature of the afterglow, and any hypothesis explaining the phenomenon at this time must be based on a rather uncertain foundation. Nevertheless, there are a few facts which give some indication of its cause. It is evident that the afterglow is not due to electronic oscillations started by the discharge and which die down slowly, because Lorentz, in discussing the theory of radiation,[1] cites the interference experiments of Michelson and Lummer and points out that the time required for a vibrating electron to lose half its energy, as shown by its radiation, is exceedingly small. The radiation is reduced to half its original value after forty million vibrations, and since the number of vibrations of yellow light is about $5 \times 10^{14}$ per second, the time required for the radiation to be reduced to one half its original intensity is approximately $1.0 \times 10^{-7}$ seconds. The afterglow remains visible for many minutes, therefore its long duration is obviously due to electronic oscillations which are freshly started throughout the time the afterglow continues. Thus the afterglow at any moment must be the total radiation from a great number of separate electronic disturbances, the same being of very short duration, the diminishing number of such new disturbances in each succeeding second determining the rate of decay of the afterglow. If the afterglow is connected with a polymerized state of the gas, as suggested by J. J. Thomson, then the electronic disturbances would correspond to separate reconversions of the unstable chemical compound as the gas gradually returns to its normal state. According to the writer's experiments, the duration of the afterglow depends on the pressure in a marked manner, and since the intensity is also affected, it is probable that the intensity as well as the duration are both connected with the number of collisions that are taking place in the gas. It would appear, therefore, that the reconversions of the chemical compound referred to are started by the collisions of the gas particles. Burke's observation that the afterglow conducts electricity after the ions have been driven out by an applied E.M.F. can be explained on the hypothesis that fresh ionization, accompanying the chemical changes in the gas, takes place all the time the afterglow is present.

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[1] Lorentz, Résultats et problèmes de la théorie des électrons. Archives Néelandaises des Sciences Exactes et Naturelles, Series II., Vol. XI. p. 52.

I wish to express my indebtedness to Professor E. F. Nichols for suggestions concerning certain parts of this work, and to Dr. Bergen Davis for giving valuable assistance relating to both the theory and the production of the electrodeless discharge.

PHŒNIX PHYSICAL LABORATORIES,
COLUMBIA UNIVERSITY, June, 1906.

# THE TEMPERATURE OF SOLID CARBONIC ACID AND ITS MIXTURES WITH ETHER AND ALCOHOL, AT DIFFERENT PRESSURES.

By John Zeleny and Anthony Zeleny.

1. Solid carbonic acid and more especially a mixture made by the addition of ether or alcohol have long been used for the maintenance of a fixed low temperature. Under reduced pressures the temperature of the substance is reduced still further, and a knowledge of the temperature assumed at any given pressure gives one the means of readily producing and maintaining temperatures between — 77° C. and — 115° C. We are not aware that any detailed study of the variation of the temperature of the above mixtures with pressure has been made, although du Bois and Wills[1] have obtained the temperature of the carbonic acid snow itself at several pressures.

There are differences of opinion among the different writers as to the effect of adding ether or alcohol to the carbonic acid snow, and the value of the temperature is usually given without any regard to the effect of changes in the barometric pressure. There is disagreement, too, among the values given for the temperature of the carbonic acid snow itself at atmospheric pressure.

Cailletet and Colardeau[2] give — 60° C. for the temperature of carbonic acid snow at atmospheric pressure, and — 76° C. as the temperature in a good vacuum. For a mixture of carbonic acid and ether at atmospheric pressure they give the value — 77° C., and for the temperature of the mixture in a good vacuum they give the value — 103° C. For a mixture of carbonic acid and alcohol the value given by them is — 72° C.

Regnault[3] gives — 78°.16 for the boiling point of carbonic acid. Villard and Jarry[4] give the temperature as — 79° C. and state that

[1] Beibl. zu d. Annal. der Physik, 24, p. 428.

[2] Jour. de Physique (2), 7, p. 430.

[3] Ann. de Chim. et de Phys. (3), 26, p. 259.

[4] Compt. Rend., 120, p. 1413.

the variations due to the changes of the barometer are insignificant, although at a pressure of 5 mm. they found the temperature of the snow to be — 125° C. They state that at atmospheric pressure no change in the temperature was produced by adding ether to the snow.

Du Bois and Wills[1] give the temperature of carbonic acid snow at atmospheric pressure as — 79°.2 C., with a rate of change of 1° C. for a change of 55 mm. in the pressure.

For the temperature of a mixture of ether and carbonic acid snow Travers[1] ascribes to Olzewski the value of — 78°.2 C. Witkowski[2] gives — 78°.5 C. for the same mixture. Holborn[3] found the temperature of a mixture of absolute alcohol and carbonic acid snow at atmospheric pressure to be — 78°.34 C., with a variation of 0°.20 for a change of 1 cm. in the pressure. Carbonic acid snow itself gave a temperature 0°.10 C. lower.

2. In the experiments here described the carbonic acid snow was obtained from a cylinder of commercial liquid carbonic acid. The temperatures were measured by means of a nickel-iron thermo-electric couple. This was calibrated by the use of six known temperatures. The two temperatures used upon which the values given in this paper mainly depend are: (*a*) the value given above which Holborn obtained with a hydrogen thermometer for the temperature of a mixture of absolute alcohol and carbonic acid snow, and, (*b*) the temperature of boiling ethylene which was taken as — 103°.9 C. for a pressure of 74.0 cm.[4] The measurements were made with a D'Arsonval galvanometer which, with the scale at a distance of 2.6 meters, enabled the temperature to be read to 0°.01 C. The couple was short-circuited after each deflection and the reading taken so as to eliminate the errors due to any thermo-electric forces in other parts of the circuit. Errors due to either a set in the fiber or to hysteresis[5] were eliminated at the same time. The changes in the room temperature were too slight to necessitate any correction for temperature.

[1] Study of Gases, p. 245.

[2] Phil. Mag., (5), 41, p. 301.

[3] Annal. der Physik., 6, p. 245.

[4] Travers, Study of Gases, p. 243. (Wroblewski, Witkowski, Ramsay and Travers.)

[5] A. Zeleny, PHYS. REV., 1906, vol. 23.

3. (*a*) Attention was first directed to the temperature of carbonic acid snow contained in an open vessel. It is known[1] that to maintain a constant temperature the snow must be surrounded by its own vapor. A glass beaker was nearly filled with the snow and the thermo-electric junction was placed in its center.

As long as the windows of the room were closed and the air was well at rest the temperature of the snow in the beaker remained quite constant at its normal value, but the presence of any draughts at once lowered the temperature appreciably. Blowing past the beaker with a bellows and thus rapidly removing the vapor caused the temperature to decrease by over 15° C.

A piece of the snow placed over the junction and held above the table so that the vapor formed could flow downward from the solid had its temperature reduced by over 10° C. below the normal temperature.

A deep vessel only partly filled with the snow and preferably corked so as to leave but a small vent, answers best for maintaining a constant temperature. The snow must however be well packed so as to make a good contact with the junction or else a slightly too high temperature is obtained. On the other hand the stirring caused by the act of packing down the snow seems to increase the rate of evaporation and causes a small temporary diminution of the temperature.

(*b*) In the next place a mixture made of ethyl ether and carbonic acid snow was placed into the glass beaker. The temperature of this remained very constant, unaffected by slight draughts; and the blowing of a strong blast with a bellows by the mixture barely diminished its temperature by 0°.02 C. It seems that the heat received from the air blast almost exactly equalized the cooling due to the more rapid evaporation caused by the removal of the vapor. After the blowing had been continued for some time, however, the uppermost parts of the surface became whitish as if the ether had all evaporated from them and exposed the clear snow. When this point was reached the evaporation was accelerated and the mixture began to cool just as it had done in the case of the dry snow; and by continuing the blowing the temperature of the whole was reduced by several degrees.

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[1] Faraday, Phil. Trans., 1845, p. 155. DuBois and Wills, loc. cit.

Under normal conditions however the temperature of the ether mixture is remarkably constant,[1] as long as the snow is moist and as long as there is not enough ether present for a liquid surface to form over the snow.

Stirring the mixture had a tendency to produce a temporary lowering of the temperature by about 0°.02 C. When the mixture is first made a temporary lowering of the temperature by as much as 0°.5 C. was observed. This always disappears soon, however, and may be due to some of the snow dissolving in the ether.

(*c*) A mixture was next made of absolute alcohol and the carbonic acid snow, and placed into the glass beaker. To assume its lowest temperature this mixture must be quite thick, much more so than is necessary with the ether mixture. There should be no appearance of any free liquid throughout the mass of the mixture. Blowing a strong blast of air past the mixture with the bellows caused a rise in temperature of about 0°.2 C. The cooling due to the increased rate of evaporation at the surface is not sufficient in this case to equalize the heat received from the air blast. An increased ebullition in the interior of the mass however prevents the temperature from rising very far. When the blast was continued, the heat from it vaporized so much of the carbonic acid in a short time, that the mass became too moist from an excess of the alcohol, the ebullition became very brisk and the temperature increased quite rapidly.

(*d*) It thus appears that of the three refrigerants, dry carbonic acid snow, a mixture of absolute alcohol and carbonic acid snow, and a mixture of ether and carbonic acid snow, the last is the best one to use for maintaining a uniform temperature. The absolute temperature of the three, however, was found to be identical when they were placed in a deep vessel so as to be surrounded by their own vapor. The differences which were observed for the three at different times for the same barometric pressure did not exceed 0°.02 C.

4. The temperature of the three refrigerants was next measured when they were subjected to different pressures. In some cases

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[1] We could not observe any change of temperature when a vessel with the mixture was covered to exclude air, such as is described by Faraday (loc. cit.).

the substance was placed in a long cylindrical Dewar flask 4 cm. in diameter. The opening was closed with a rubber stopper through which the thermo-electric couple passed and from which a rubber tube led to an open mercury manometer and to a water pump. A vessel of large volume was placed in series so as to equalize some of the variations due to the inconstancy of the pump. In other cases the Dewar vessel was replaced by a glass tube of the same diameter. The advantage of this was that it could be placed inside of a large Dewar cylinder to protect it from heat but when the temperature was to be raised the tube could be withdrawn and the process greatly accelerated.

To produce pressures higher than an atmosphere the rubber tube leading from the containing vessel was partly closed by means of a screw clamp. Also in adjusting for the lower pressures the rubber tube leading from the vessel was closed by the proper amount with the screw clamp, while the water pump was operated at a constant pressure. By watching the indications of the manometer and carefully using this screw the variations of the pressure could readily be kept within a millimeter.

The temperature of the refrigerant assumes its final value much more rapidly in going from a higher to a lower temperature than in the reverse direction. In the first case the rapid evaporation quickly cools the mixture to its final temperature while in the second case the heat has to come in through the walls of the vessel. It is especially desirable, therefore, when a Dewar cylinder is used, to approach any temperature from one that is higher. With the protection of the Dewar flask the freezing mixtures evaporate but slowly even at low pressures and so any temperature can be maintained for a long time without a change of material.

5. Eight sets of readings with over a hundred observations were taken with the three refrigerants. The reduced values that were obtained were plotted on a large scale and the points for the three substances all appeared to belong to one and the same curve. It was concluded that the temperatures of the three substances at any one pressure are the same. A single curve was therefore drawn through all of the points obtained. The agreement of the observations was on the whole good although a few of the individual points

varied as much as 0°.5 from the main curve. The observations with the alcohol mixture did not extend below — 100° C.

The values of the temperatures at the different pressures was read off from the curve thus obtained and the results are given in the following table:

*The Temperature of Carbonic Acid Snow and Its Mixtures with Ether and Alcohol, at Different Pressures.*

| Pressure in Centimeters of Mercury. | Temperature. ° C. | Pressure in Centimeters of Mercury. | Temperature. ° C. |
|---|---|---|---|
| 2 | −116.7 | 44 | −85.2 |
| 3 | −112.9 | 46 | −84.6 |
| 4 | −110.0 | 48 | −84.1 |
| 5 | −107.8 | 50 | −83.6 |
| 6 | −106.0 | 52 | −83.1 |
| 7 | −104.5 | 54 | −82.6 |
| 8 | −103.2 | 56 | −82.2 |
| 9 | −102.1 | 58 | −81.8 |
| 10 | −101.1 | 60 | −81.4 |
| 12 | − 99.4 | 62 | −80.9 |
| 14 | − 97.9 | 64 | −80.5 |
| 16 | − 96.5 | 66 | −80.1 |
| 18 | − 95.3 | 68 | −79.76 |
| 20 | − 94.2 | 70 | −79.40 |
| 22 | − 93.2 | 72 | −79.04 |
| 24 | − 92.2 | 73 | −78.86 |
| 26 | − 91.3 | 74 | −78.68 |
| 28 | − 90.5 | 75 | −78.51 |
| 30 | − 89.7 | 76 | −78.34 |
| 32 | − 89.0 | 77 | −78.17 |
| 34 | − 88.3 | 78 | −78.00 |
| 36 | − 87.7 | 80 | −77.66 |
| 38 | − 87.0 | 82 | −77.33 |
| 40 | − 86.4 | 84 | −77.00 |
| 42 | − 85.8 |  |  |

It is seen that at atmospheric pressure the temperature of the mixtures changes by 0°.17 C. for a change of 1 cm. in the pressure. This rate increases as the pressure is diminished so that at a pressure of 2 cm. it is over twenty times as large.

The values given by du Bois and Wills (loc. cit.) for the temperature of carbonic acid snow are from 1° to 2° lower than those determined by us for the snow and its mixtures with ether and alcohol. Thus at 76 cm. pressure their value is — 79°.2 C. and at 4 cm. pressure, — 112° C. The differences appear to be due to the fundamental temperatures assumed for the calibration of the thermo-electric couples.

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June 29, 1906.

# MEASUREMENTS OF THE INTERNAL TEMPERATURE GRADIENT IN COMMON MATERIALS.

By Charles B. Thwing.

THAT many metals and common materials are radio-active has been established by the work of several observers. Since the radio-activity of radium compounds produces an elevation of temperature within a mass of the substance, it is to be expected that other radio-active bodies will exhibit the same phenomenon in a much smaller degree.

That the magnitude of the temperature gradient in the common metals and rocks is large enough to be detected and measured seems to be demonstrated by the experiments about to be described.

## Apparatus.

The metals were cast in the form of cylinders, 100 mm. in diameter and 25 mm. in height, two such cylinders of each substance being employed. In the case of oxides, etc., in powder form, the substance was contained in paper cartons of the same dimensions as the cylinders, having a circular opening 75 mm. in diameter in one end, which opening was closed by means of a sheet of thin waxed paper.

The thermometer consisted of 116 nickel-iron couples connected to a sensitive D'Arsonval galvanometer. The nickel wires were 0.26 mm. and the iron 0.34 mm. in diameter. The iron wire was tinned and the joints were made by soldering, rosin being used as a flux.

The couples were wound radially on a ring of mica, the inner diameter of which was 25 mm., the outer 125 mm., and were insulated and protected from moisture by a coating of wax composed of bees-wax and rosin. The entire series of couples has a resistance of 15 ohms.

The galvanometer for this work was furnished by Leeds and

Northrup. The suspensions were of silver, the resistance of the galvanometer being 25 ohms. A deflection of 1 mm. at 1 m. distance corresponds to a temperature difference in the couples of 0.0000055° C. The image of the scale was clear and the needle at rest, so that tenths of a scale division could easily be estimated.

In order that small differences of temperature might be measured it was of course necessary that the specimens and thermometer be protected from external temperature changes. This condition was quite perfectly met by placing them in an ice-calorimeter, as indicated in the figure. The inner cylinder of the calorimeter was 175 mm. in diameter and 250 mm. high; the outer cylinder was 400 mm. in diameter and 720 mm. high. The whole was contained in a barrel 830 mm. high and packed with sawdust. Heavy woolen blankets covered the top. A tube between the cylinders allowed the galvanometer leads to enter, and the outer cylinder was provided with a rubber drain-pipe near the bottom.

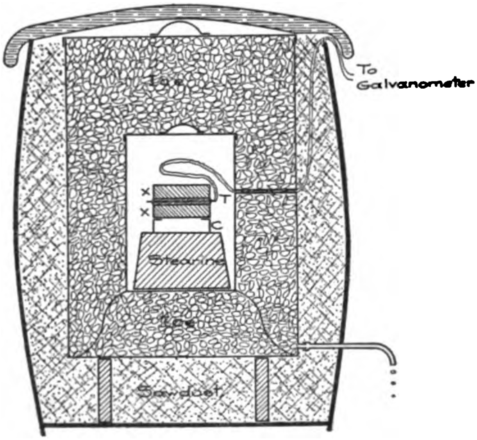

Fig. 1.

Ice was supplied on alternate days and was crowded down to the bottom of the calorimeter twice daily, about 5 kg. per day being the amount consumed. The ice was of uniform texture (artificial ice) and was said to be made from distilled water.

The galvanometer leads were of flexible copper wire, with rubber and cotton insulation, the portion entering the calorimeter being further coated with wax.

The pair of specimens, *X*, *X*, to be examined rested with the thermometer, *T*, between them upon a paper carton, *C*, similar to those used for studying powdered materials. The carton, in turn, rested upon a block of stearine which lay in the bottom of the calorimeter.

The time required for a specimen, after being placed in the calorimeter, to reach a steady temperature was from twelve to twenty hours, depending mainly on its conductivity for heat. After this interval had elapsed the deflection remained nearly constant for an indefinite period. The longest period tried was fifteen days. As a rule three or four days seemed sufficient for making a determination.

## RESULTS.

Of the substances thus far examined, all, without exception, show an internal temperature gradient. It is intended to extend considerably the list of substances included in the table. The results obtained seemed of sufficient interest, however, to justify their publication at the present time.

TABLE I.

| | Deflection. | $t$ | $t$/cm. |
|---|---|---|---|
| Lead | 5.4 | 0.000059 | 0.000020 |
| Antimony | 3.9 | 0.000043 | 0.000014 |
| Zinc | 3.1 | 0.000034 | 0.000011 |
| Iron | 2.9 | 0.000032 | 0.000011 |
| Copper | 2.8 | 0.000031 | 0.000010 |
| Aluminium | 4.1 | 0.000045 | 0.000015 |
| Aluminium oxide | 28.0 | 0.000308 | 0.000103 |
| Magnesium oxide | 16.1 | 0.000176 | 0.000059 |
| Marble | 1.4 | 0.000015 | 0.000005 |
| Sandstone | 7.2 | 0.000079 | 0.000026 |

The second column gives the definition in mm. with the scale 50 cm. distant. The third column gives the temperature 3 cm. within the specimen when the surface and surroundings are at 0°. The fourth column gives the gradient in degrees per centimeter.

## SOURCES OF ERROR.

The most obvious sources of error are (1) thermo-electromotive-forces in the galvanometer itself or in the leads; (2) chemical electromotive forces due to moisture in the insulation of the elements; (3) variations in the temperature of the calorimeter.

Concerning (1) it was found that during rapid changes of temperature of the room a deflection was observed if the galvanometer was short-circuited through the lead wires. This deflection depended upon the direction of change of room temperature and was divided by 2 if a resistance equal to that of the galvanometer was added to the circuit. Under ordinary conditions this error was not above 1 or 2 per cent. of the observed deflection. Cooling the joined ends of the lead wires 15° or heating them a like amount produced no deflection.

Concerning (2) it is to be observed that the order of nickel and iron in the thermo-electric series is opposite to their order in the contact series, so that any leakage between the elements would produce a deflection opposite in sign to the deflection observed. A leak between the last iron element and the copper lead wire might produce a deflection in the same direction as the one observed.

Concerning both (1) and (2) it remains to be said that any currents due to the sources mentioned should not be dependent upon the presence of the specimens surrounding the thermometer but should be equally in evidence when no specimens are present. It is found, moreover, that when the thermometer is exposed alone in the calorimeter, resting upon the rim of the paper carton, no deflection save a small one of variable sign is observed.

In regard to (3) it was found that the temperature of the calorimeter was raised by about 0.00001° to 0.00002° by the melting of the ice away from the bottom of the inner cylinder during the 12-hour intervals between the times of packing down the ice. This was shown by a rather rapid increase of the deflection immediately following the packing followed by a slow return to the first reading.

In brief, there seems to be no source of error present when the specimens are in place which is not equally present when they are removed. When the specimens are removed deflections as large as 1.0 are observed. With the specimens in place deflections corresponding to a negative gradient are never observed, and the variations observed never exceed 20 per cent. of the total deflection. It seems certain, therefore, that the values given in the table represent the gradient under the conditions described to within from 10 to 20 per cent.

## CONCLUDING REMARKS.

The obvious explanation of the observed phenomenon is, of course, to assume that the temperature is due to radio-activity, either of the substance itself, or of radio-active substances contained as impurities. It seemed not out of the range of possibility that oxidation of the surfaces of the specimens might generate a measurable amount of heat. It was found, however, that boiling the iron cylinders in purified vaseline and testing them with a film of the vaseline still on them showed no variation in the results. The vaseline used is remarkably free from either acid or alkali and does not corrode metals immersed in it for many months.

Substances, moreover, like MgO or $Al_2O_3$ can hardly be thought of as undergoing any chemical change during the experiment.

The order of magnitude of the temperature gradient in different substances does not, of course, indicate the order of their radio-activity, since the heat generated is conducted away more rapidly in good conductors like copper and aluminium than in the more poorly conducting metals and oxides.

The magnitude of the temperature gradient found is more than sufficient to account for the known temperature gradient below the surface of the earth on the assumption made by Rutherord in his criticism of Strutt's results that the entire mass of the earth is radio-active to the same extent as the portions found near the earth's surface. Since, however, the values for the radio-activity of substances at the surface of the earth found by different observers using widely different methods all agree in being too large to be explained on this assumption, it may be worth while to consider another hypothesis, *viz.*: that the radio-active materials are to be found mainly in the earth's crust.

On the hypothesis that the elements have evolved somewhat in the order of their atomic weights under conditions of increasing agglomeration of the particles composing the gravitating mass, it might appear that the chief condition for stability of the complex atoms was enormous pressure, a condition better fulfilled far below the earth's surface than at the surface. Elements, therefore, which at a later period found themselves nearer the surface of the earth than at the period of their birth might be expected to show radioactivity.

The body of observed facts is as yet far too meagre to justify anything more than the merest speculation upon this most fascinating subject. It would seem, however, that henceforth the geologists may be permitted to claim such periods for the life of the earth as their various theories demand without fear of contradiction from physicists.

It is the writer's intention to extend the list of substances examined and to check the observations by control experiments, some of which are now in progress.

I desire to express my thanks to the American Academy of Arts and Sciences for appropriations from the Rumford Fund covering the expenses of the investigation, and also to the President and Director of the Physical Laboratory of Adelbert College, who have placed at my disposal a very suitable room and all available facilities for carrying on the work.

PHYSICAL LABORATORY OF ADELBERT COLLEGE,
WESTERN RESERVE UNIVERSITY, CLEVELAND, OHIO,
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# THE PHYSICAL REVIEW.

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## A SPECTROPHOTOMETRIC STUDY OF SOLUTIONS OF COPPER AND COBALT.

By B. E. Moore.

### I. Introduction and Object of the Investigation.

THE color of substances in solids or in solutions has been the subject of many investigations and its literature is very extensive. Many important features are observed by the unaided eye. Such, for example, are the complementary colors of transmission and reflection, and the change in absorption due to change in thickness. The instruments used in the study of color are also numerous. The methods are colorimetric, photographic and spectrophotometric, or these methods in combination. The latter only gives accurate quantitative measurements of absorption. All methods have features to commend them. The first step beyond the use of the unaided eye is the use of the spectroscope and eye to mark the region of absorption. Bunsen[1] and others early used this method. By means of cross wires the region between light and dark is determined. This method has been extensively used by Ostwald[2] and Hartley[3] who arrived at diametrically opposite conclusions upon the conditions of substances in solution. Both combine the method with the photographic process which leaves a permanent record of the character of absorption. Hartley modifies his observations by resorting to the common method of placing the absorbing solution in a wedge-shaped vessel whose angle is at right angles to the refracting angle of the spectroscope prism. By this means he obtained spectral absorption showing different intensity at top and bottom, and a sloping curve across limited portions of the spectrum. The slope indicates the sharpness of the absorption. This method is an excellent one to give a comprehensive view of absorption, and, apparently, was so regarded by Ostwald; but it is possible to overestimate its value. Hartley appears to do this. In his criticism of Ostwald's work he emphasizes the importance of a sharp location of the band. Now, it is clear that the absorption bands shade off into the light regions by degrees. There is no discontinuity approaching that of the line spectrum; consequently, a difference in concentration may cause the same darkening as an increase in temperature does in some of Hartley's experiments. So that it is here necessary to use precaution in making fine distinctions. The most important thing, however, in color study is the determination of the absorption throughout the whole spectrum band, and nominally transparent region, for upon the intensity of absorption, as well as the position, the color depends. The spectrophotometric method involves a quantitative matching of two beams of light, one of which is reduced in intensity by passage through the absorbent. The instruments used for this work are also numerous, but those using the principle of a vanishing line when intensities are equal are superior to those which require the observer to judge equal illumination. With the eye the spectral limits of observation are limited, only the central region of the spectrum can be observed. The photographic record can be taken much farther in the short waves. A combination of photographic and spectrophotometric is here possible. The rays of different intensities have varying degrees of action upon photographic plates, and these plates may afterwards be examined for absorption when there may be obtained quantitative results of a high order of accuracy.[4] The thermopile, or, better, the bolometer, or the radiometer, is also a commendable method for quantitative study. These are particularly applicable for waves longer than the eye can measure.[5] These methods of study may be used for various purposes. A pure product may have a certain color or absorption and the same product in an impure or inferior form quite different absorption. The method may be used to study the law of absorption. Beer's law requires that the ratio of transmitted light shall be equal to $e - kcl$, where $c$ is the concentration, $l$ the thickness and $k$

a constant, sometimes designated as the extinction coefficient, depending upon the wave-length and nature of the absorbent. The reasons for the Beer's law are apparent and its confirmation in such substances as colored glasses or solutions where thickness only varied, was an easy matter, but the early literature shows no such agreement when the concentration of solution varied. Some confirmed the law; others did not do so. There were two reasons for non-confirmation: Firstly, some of the methods of measurement were not sufficiently refined; and, secondly, and more important, there were changes in the character of the solutions when concentration changes occurred. When the theory of solution developed so that this fact was recognized, Beer's law became an important so that this fact was recognized, Beer's law no longer became the point of strife, but the changes in color, and, consequently changes in the coefficient in Beer's law became an important index of the changes of solution, *i. e.*, color methods of study became an important method of studying the physical and chemical properties of solutions, *e. g.*, the change from the molecular to the ionic condition in dilute solutions. Ostwald[2] clearly outlined this phenomenon when he enunciated the law that substances which contain a common colored ion have a given color in dilute solution.

The outline in the present experiment was to follow some of the color changes by the spectrophotometric method. This method requires, generally, observations at several points in the spectrum. It is, therefore, somewhat tedious and irksome in comparison with other spectral methods, or even in comparison to kindred methods of approaching the same question; *e. g.*, the freezing-point method, or electrolytic conductivity methods. The work is as many times greater as there are points studied in the spectrum. To this must be added repeated observations to be sure of accuracy. Color changes are sometimes apparent enough, but of small magnitude. Under such circumstances the most that can be obtained from quantitative measurements is qualitative results. Results in spectrophotometry have, generally, been of this type; *i. e.*, they were indicative only of general processes in solution. That is, quantitative calculations can not be made from quantitative readings like it is possible to do in electrolytic measurements or freezing-point determinations. A recent attempt by Vaillant[6] to make results quantitative have been attended by considerable success. He gives errors in results as large as 10 per cent. This does not mean errors of that magnitude in the spectrophotometric measurements, but errors arising from an application of the exponential formula. The present author followed quantitatively the hydrolysis of ferric chloride[7] by means of the spectrophotometer. The exponential formula was necessary here also. This led the author to the conviction that spectrophotometric observations need several times their present accuracy before thoroughly reliable quantitative calculations can be made. But, withal, the method is a great advance over the method of mapping absorption fields. A number of observers have followed the changes upon diluting water solutions, spectrophotometrically, and have generally confirmed the dissociation hypothesis. Vaillant[6] alone seems to have made a thorough quantitative comparison of dissociation, obtained from electrical data, with the absorption. In general he found a close parallelism between the observed and the computed absorption. There were marked differences in some concentrated solutions, which suggest the presence of other products. These he calls hydrates, but in the course of this paper it appears that these may be other products. The work upon permanganates may be mentioned here, inasmuch as Hartley[3] dissents from the conclusions drawn by Ostwald[2] upon these solutions. Hartley retains the conception of the complete integrity of the molecule — an opinion which he confesses to have formed before the theory of ionic dissociation was developed; and, farther, maintains that salts containining water of crystallization still contain this water in solution as an integral part of the molecule. Then he adds to this the physical theory of absorption,[8] *viz.*, that absorption arises from molecules whose periods of vibration are the same as the light which they absorb; and draws the conclusion that molecules vibrate as a whole or as units, showing an absorption which depends upon the period of vibration. A change in weight of the molecule must change the period and there must be some shift of the absorption bands. In the permanganates Ostwald marks the position of four bands (instead of one band, as Hartley reports), and all retain, practically, the same position for all salts in dilute solutions. Hartley contends for a greater dispersion when there is so little difference in the weight of the salts in the electropositive series as in these permanganates. Such a process means, in general, a lack of definition.

Pflüger,[11] Vaillant[6] and the present writer[12] studied these salts spectrophotometrically. Pflüger's work covered eleven salts of great dilution at one point in the spectrum, *viz.*: at 576 $\mu\mu$, and at the same point in the spectrum he also studied solutions of $Na^-$, $K^-$, and $Ba^-$ permanganates of 1,000 times as concentrated as the dilute solutions. Taking into consideration the degree of dissociation the latter three all show the same absorption coefficients. Vaillant studies $K^-$, $Ba^-$, and $Zn^-$ permanganates at four different points in the strong absorption region. These were studied at several concentrations, but mostly of great dilution. From the electrical conductivity of all, and the absorption of one the absorption of the other solutions may be calculated. The absorption so calculated agrees well with the observed values, and hence the conclusion that the absorption depends upon the ionization. The data for the more concentrated solutions show values of absorption for the molecules slightly different from the ions and also slightly different from each other. It was possible for the molecules to have all absorbed alike. Vaillant contends that the variations could just as well arise from variation in the state of hydration of the molecules as from the ionization. The general agreement with the ionic theory observed by these experimenters, does not answer the objection of Hartley. The present writer followed the absorption throughout the entire spectrum, taking readings about every 10 $\mu\mu$ in the principal absorption regions, and in the region between the principal absorption and the nominally transparent portion of the spectrum. The readings were limited to two salts $K^-$ and $Zn^-$ permanganates in concentrated and in dilute forms. Although very limited in the number of salts studied, the spectral study was very complete and could answer Hartley's contention so far as these salts were concerned. The experiments suggested the Ostwald theory but were not conclusive. In the bands the zinc concentrated and dilute and the potassium dilute were practically identical. The potassium concentrated alone differed, and this was a small difference in intensity but not in position. The concentrated zinc was about one fourth the concentration of the potassium. In the nominally transparent region the dilute solutions absorbed more than the concentrated, and were nearer equal to each other than to the concentrated, and also nearer than the concentrated were to each other. The identity of the solutions throughout the spectrum seemed to be possible, but it was not a necessary conclusion. Yet, there was a certainty of identity in position of the absorption bands, for which Hartley[3] contends.

The law of mass action requires that the introduction of an ion into a solution containing an identical ion, will repress the latter to a greater or less extent into the molecular condition. When such an ion is colored, this action, if present, may be followed spectrophotometrically. It occurred to the writer that substances in dilute solution could thus be forced to return to their form, and, therefore, to the absorption, in concentrated solutions; and possibly to obtain, even, solutions with less ions than the original concentrated solution. With this hypothesis the writer mapped out a study of the salts of cobalt, copper and nickel. As then outlined these salts were to be studied in concentrated and dilute water solutions and with acids having an ion in common with the negative ion of these salts. This treatment of the copper and cobalt salts was reported to the St. Louis meeting of the Physicial Society in September, 1904. It was then suspicioned that certain irregularities could be explained by variation in the concentration of the acids and the presence of hydrates in solutions as outlined by Jones and colaborers. Hence the scope of the work was broadened to treatment of diluted solutions in acids of varying concentrations and in salts containing the same negative ion as the dilute solution.

In the past year the pressure of other work has only permitted the application of this principle to cobalt sulphate and cobalt chloride. The other results are the same as reported at St. Louis, except that they have all been repeated. The results already obtained indicate the desirability of applying the method to the substances originally contemplated, but unforseen events in the department of Physics make it impossible to take up the work before, at least, another year; so that, rather than delay for completion, the present work is sent to the press. If the present results indicate possibilities or stimulate further inquiry, the work will have some value.

The plan of mixtures and a change in the solvent has been followed by Vaillant[6] in a very comprehensive spectrophotometric investigation. Many of the substances and mixtures herein studied were also studied by Vaillant. He studied more solutions and computes absorption coefficients from a comparison with the electrical data. His observations were limited to a few points in the spectrum, generally three within the band and close together, but sometimes as many as six points. The writer has studied many less solutions, but has observed throughout the spectrum, trying to make the spectrophotometric observations complete. So that, what one observer has done the other has left undone. The solutions are different in all respects except in name. The treatment is generally different. The discussion is radically different. The present writer had in mind during the progress of the experiments some investigations made about the time of Vaillant's publication and subsequent thereto.

## II. Experimental Method.

The Brace Spectrophotometer[14] was used throughout the experiments, and the method of using and adjusting it was the same as in other contributions. Therefore the following brief description will suffice. In Fig. 1, the light from the opposite sides of a small isolated section of a flat acety line flame passes on the left through a tube $T_1$, lens $L_1$, reflected from mirror $M_1$, focussed upon slit $S_1$, thence through the collimator to prism $P$, and lastly to the observing eye at the telescope $O$. The light upon the side passes through a similar path, but within the prism is reflected from a silver strip and thence through the telescope $O$. The two fields are adjacent, with a line which vanishes when the fields are matched in intensity. The slit $S_2$, was fixed at about .8 mm. in width. The slit $S_1$ was variable and read with the telescope $O'$. Generally the absorbent was placed in the position $T_2$ and no tube placed in the

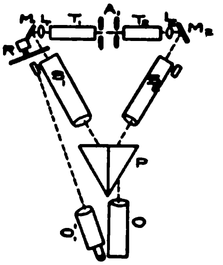

Fig. 1.

position $T_1$. $T_1$ was generally filled with the same product as $T_2$ except that the colored component was omitted. This tube was then placed in the position $T_2$ and the slit $S_1$ adjusted for a match at the point of the spectrum wished. Tube $T_1$ is next replaced with tube $T_2$ and a new setting of the slit made.

To avoid large changes in $S_1$ and, consequently, the calibration of the slit, a rotating sector was used in connection with the slit. The latter was always adjusted so that the slit $S_1$ need be closed only a small per cent. The ratio of the intensity of the beams transmitted by the tubes $T_2$ and $T_1$ is thus measured. This is readily seen to be the per cent. of light transmitted by the colored component only, without any corrections whatsoever. For very transparent portions of the spectrum the first setting of the slit $S_1$ is made with tube $T_2$ in position $T_1$, and $T_1$ in position $T_2$ and a small absorbent placed before $S_2$ so as to avoid opening $S_1$ beyond its normal width. The tubes are then interchanged and another setting made. These tubes were made in pairs; the shortest pair was each 10 mm. long; the longest pair 300 mm. long. Reversing the position gave length up to 600 mm. Concentrated solution in strong absorption region was studied in wedge-shaped vessels. These were usually about .1 mm. (platinum) on one end, and about .85 mm. (tinned pins) on the other end. The transmission walls were of plate glass, uniformly clear, and about 10 mm. thick. A glass plate bottom was sealed on the outside with laboratory cement. By observing through two different thicknesses the absorption arising from increased thickness is obtained. This thickness is determined from the slope and the horizontal displacement. The end plates of the tubes were fastened by paraffin to the tubes on the outside, which while still warm is drawn by capillarity between the ground end of the tube and the plate. The plates are then held by clamps. These end plates were selected with regard to their optical uniformity, but to keep them optically clean proved about the most tedious part of these experiments. In the study of cobalt sulphate, mixed with sulphuric acid, but one tube was used. Readings were taken throughout the entire spectrum with acid and then with the tube filled with cobalt and acid mixture. This required less care and generally expedited matters, but sacrifices some in accuracy. Generally five readings were taken for the first setting of the slit, ten for the second setting, and again five for the first.

Color measurements were made at the temperature of the room, which varied from 20° C. to 25° C., but usually from 23° C. to 25° C. This temperature change could be of little importance unless in cobalt chloride. The acid solutions of this salt were studied in very warm weather, when the temperature ranged from 25° C. to 27° C. All chemicals used in these experiments were purchased from the Mallinckrodt Chemical Works of St. Louis, and marked chemically pure. The crystals of the copper salts were washed and then dissolved in warm double distilled water and allowed to precipitate by cooling. From the crystals so obtained the solutions were made. After long standing, new stock solutions were required. Cobalt solutions were made from the purchased samples. To determine densities a calibrated Mohr's balance was considered sufficiently accurate. The water used in all cases was double distilled. The per cent. of salts in solution was obtained, when possible, from Landolt's & Bernstein's Tables; in other cases it was necessary to make a quantitative chemical analysis of the solution. From per cent., densities and molecular weight values (oxygen equal to 16 in these tables), the equivalent concentration is computed. The solutions were diluted by means of an accurately calibrated pipette (5 c.c.) and flasks with small necks.

Beer's law is used to reduce the observations through different lengths and in various concentrations to a common basis. Using $A$ as the reciprocal of $K$ in Beer's law, we have

$$A = \frac{cl}{\log \frac{i_0}{i}}$$

where $i$ is transmitted light and $i_0$ the incident light, $C$ the equivalent concentration, and $l$ the length expressed in millimeters. $A$ is that thickness in millimeters of a solution of one equivalent which transmits 10 per cent. of the incident light. This may be called the equivalent transmission coefficient. I have generally used this term instead of its reciprocal, $K$, designated the equivalent extinction coefficient. Although many data are published in terms of $K$, I have made the change because the term extinction coefficient is frequently used in optics with another meaning. Further, the thickness required to cut out a certain portion of the light is just as comprehensive, if not more so.

In the tables, the first row gives the concentration of the salt under study; the second row gives the concentration of the acid or transparent salt used. Zero acid means a water solution. The wave-lengths in $\mu\mu$ are recorded in the first column; the values of $A$ in the other columns. The latter correspond to the concentrations under which they are placed.

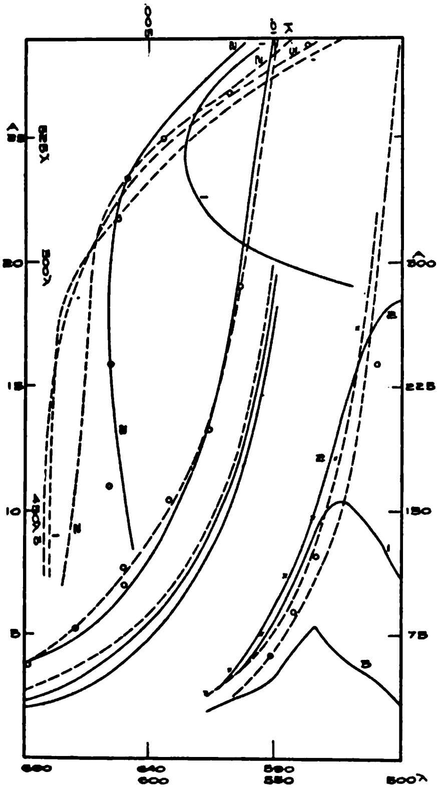

Fig. 2.

Fig. 2 gives a graphical presentation of the copper solutions. The continuous lines refer to the copper chloride solutions; the broken lines to the copper nitrates. The small "*x*'s" and circle "*o*'s" refer to the readings for the concentrated and dilute copper sulphates respectively. These substances are shown on three different scales on account of great changes. In the blue the reciprocal of *A*, *viz.*, the equivalent extinction coefficient is plotted.

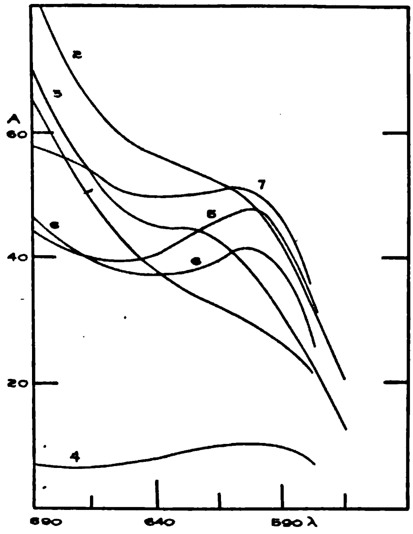

Fig. 3.

Fig. 3 gives the red end of the spectrum for water solutions of all the cobalts. The numbers have the following significance, *viz:*

1, $\frac{1}{2}$ $Co(NO_3)_2 = 5.45$
2, $\frac{1}{2}$ $Co(NO_3)_2 = .0545$
3, $\frac{1}{2}$ $Co(NO_3)_2 = .0545$ + acid
4, $\frac{1}{2}$ $CoCl_2 = 6.8$
5, $\frac{1}{2}$ $CoCl_2 = .034$
6, $\frac{1}{2}$ $CoSO_4 = 4.85$
7, $\frac{1}{2}$ $CoSO_4 = .0485$

Fig. 4 refers to the blue end of the spectrum of dilute solutions of cobalt in water. The curve shows the cobalt nitrate; the crosses "*x*" and the rings "*o*" show the cobalt sulphate and cobalt chloride respectively. Figures 5 and 6 give the red and blue spectra respectively of the cobalt chloride solutions. Figures 7 and 8 are the red and blue spectra respectively of the cobalt sulphates. The numbers on the curves, in all cases, refer to the columns in the corresponding tables. For example, in Figs. 7 and 8, take the number 8; it is a curve for the column of data under eighth *A* of Table VIII. of cobalt sulphates. Where the concentration ½(CO — $SO_4$) is .0243 and the concentration of ½$H_2SO_4$ is equal to 21.3. In all tables the observations in parenthesis correspond to one set of readings only. The other results are the mean of three determinations. In the treatment of cobalt, chloride and sulphate, with strong acids, the mean is for different concentrations of cobalt and constant strength of acids.

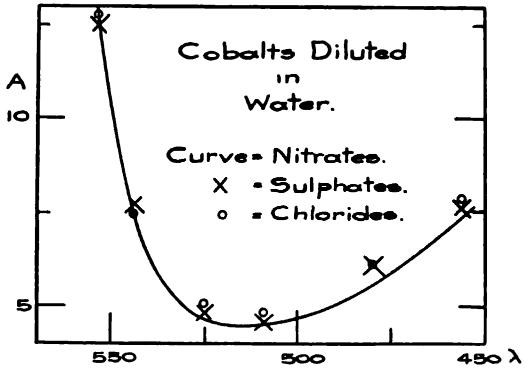

Fig. 4.

### Table I.

½$CuSO_4$.

| ½$CuSO_4$<br>½$H_2SO_4$<br>λ | 2.86<br>o<br>*A* | 2.693<br>o<br>*A* | 2.63<br>o<br>*A* | 2.596<br>o<br>*A* |
|---|---|---|---|---|
| 690.0 | 4.24 | 4.32 | 3.90 | 4.10 |
| 669.0 | 5.46 | 5.56 | 5.38 | 5.45 |
| 650.0 | 7.27 | 7.48 | 7.36 | 7.20 |
| 632.5 | 10.1 | 10.6 | 10.8 | 10.1 |
| 616.5 | 14.6 | 13.5 | 13.8 | 14.5 |
| 602.5 | 20.1 | 21.0 | 21.1 | 20.0 |
| 589.6 | 28.5 | 26.4 | 30.3 | 28.3 |

The solutions in Table I. are all freshly prepared, *i. e.*, no more than a few days old and made by methods previously described. They were also made on widely different dates. Their mean value is incorporated in Table II. under concentration 2.63. Their variation represents the degree of accuracy obtainable. The rest of

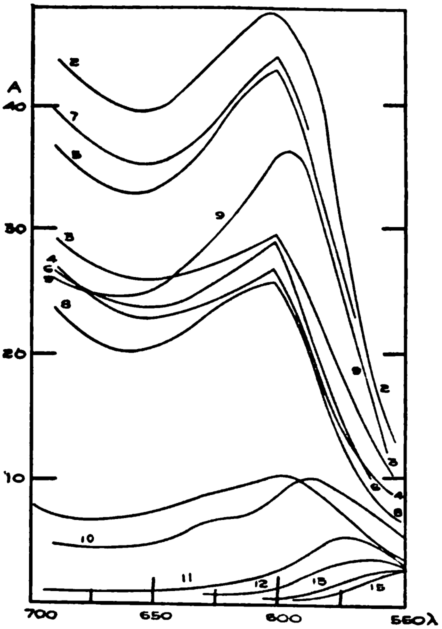

Fig. 5. CoCl$_2$.

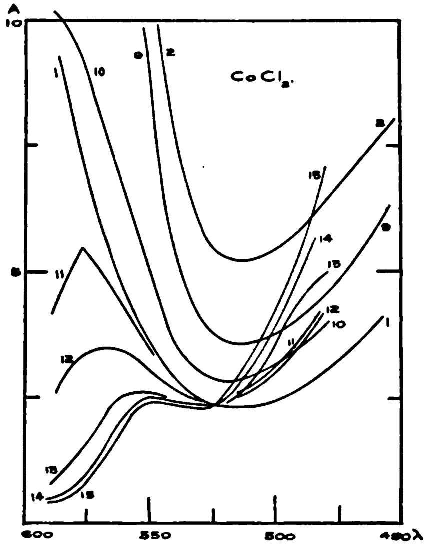

Fig. 6.

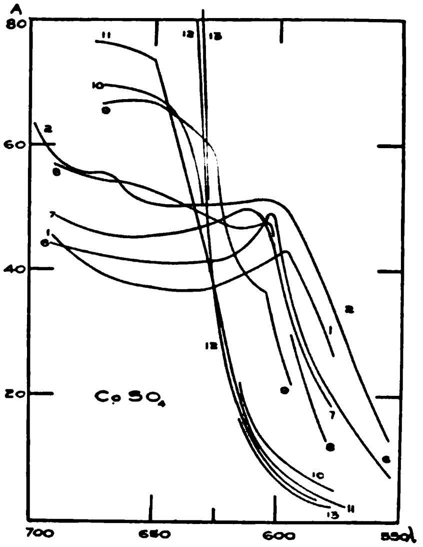

Fig. 7.

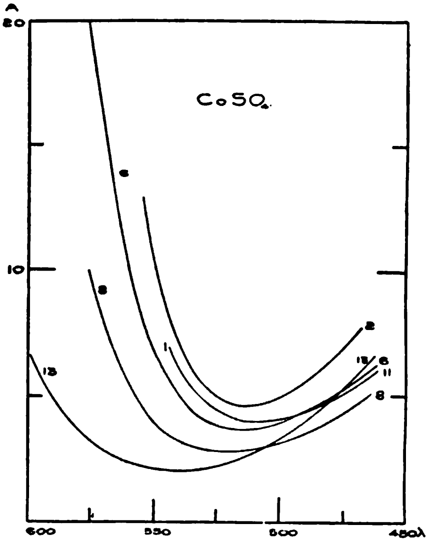

Fig. 8.

Table II. corresponds exactly to the concentrations there given. The results are the mean of three different sets of readings. It was necessary to use liquid columns of three different lengths in the different parts of the spectrum. Consequently, the spectrum could not be completed in one period of observation. When the dilute solutions stood for a day or longer there seemed to be changes, but these had no uniformity in their nature. Sometimes the solution would become more transparent, and at other times more opaque. This was particularly noticeable in the copper nitrates. The author therefore decided not to trust old solutions, but to make up fresh diluted solutions to finish uncompleted observations. In the last two columns of Table II. alone there were twelve such solutions prepared.

TABLE II.

½$CuSO_4$.

| ½$CuSO_2$<br>½$H_2SO_4$<br>$\lambda$ | 2.63<br>o<br>*A* | .0526<br>o<br>*A* | .0526<br>5.08<br>*A* | 1.232<br>o |
|---|---|---|---|---|
| 690.0 | 4.14 | 3.97 | 4.23 | |
| 669.0 | 5.46 | 5.35 | 5.41 | |
| 650.0 | 7.33 | 7.65 | 7.52 | 7.4 |
| 632.5 | 10.4 | 10.45 | 11.6 | 10.6 |
| 616.5 | 14.1 | 14.3 | 15.6 | 14.9 |
| 502.5 | 20.6 | 19.1 | 24.0 | 21.3 |
| 589.6 | 28.4 | 28.7 | 35.6 | 31.2 |
| 577.0 | 40.7 | 40.6 | 40.6 | 43.5 |
| 564.5 | 57.2 | 53.0 | — | 69 |
| 553.5 | 78 | 63.2 | 63.2 | 100 |
| 543.5 | 111.4 | 88.6 | 91.2 | 125 |
| 534.0 | 150.6 | 122.4 | 175.2 | 182 |
| 525.0 | 190.6 | 182 | 285.3 | 263 |
| 517.0 | 265.8 | 248.9 | — | 400 |
| 509.0 | 283.4 | 268.9 | — | 555 |
| 494.0 | — | — | 415 | |
| 479.5 | 293 | 286.9 | — | 2000 |
| 468.0 | — | — | 443 | |
| 456.0 | 319 | 288.2 | | |
| 436.0 | — | 251.8 | | |

Grünbaum [15] states that it is necessary to filter repeatedly in order to remove dust from the solutions. The author has not found nor heard of a process of filtering that will make solutions optically clear. Spring states that a colloid hydrate will do so. However, a sample of copper sulphate taken from the stock which has stood a day generally shows less diffusion in strong light than a repeatedly filtered one. Distilled water will also show diffusion. A satisfactory solution is the reduction of this diffusion to a minimum in the absorption and comparison tubes and then assume it to be the same in the two tubes. Copper nitrate in dilute solutions certainly decomposes and the behavior of dilute copper sulphate solutions on standing suggested the same phenomena. Hence the author's distrust of old diluted solutions. Sometimes in the transparent region it was easy to get variable readings with solutions as prepared when first added to the absorption tubes, but after half an hour standing the readings were constant. Readings were seldom taken before an hour, and solutions always stood twice that long before a set of readings could be completed.

In Table II., last column, is given data interpolated from the curve of Grünbaum's data[15] and reduced to the same basis as the author's readings. His readings were selected rather than those of Müller[16] or Ewan[17] because they extend much farther into the absorption bands. Copper sulphate is selected because concentration changes make no important difference. These readings agree well, where absorption is large, but in the regions of great transparency differ enormously. Grünbaum's hypothesis, before-mentioned, of dust in suspension is not tenable, for upon dilution the discrepancy is greater, whereas the water tube should contain a trifle more diffusion than the other, and hence an action towards increasing the apparent transparency. Müller's limited data agree well with those of Grünbaum's and both differ from Ewan by 40 per cent. in this region. The author cannot attribute the remarkable variation to difference between old and new diluted solutions, inasmuch as he knows nothing about the experience in this respect of Messrs. Ewan, Grünbaum and Müller. Neither did he make a study of old solutions for apparent reasons. If he even conceded an error in his absolute values the phenomena has evidently entered the sulphate, chloride and nitrate of copper in an identical way, and in no wise affects the results for comparison and conclusion.

In the concentrated sulphuric acid solutions, and slightly in the nitric acid solution, there was trouble due to minute air bubbles in suspension which caused dispersion in the transmitted light. These get into solutions in mixing and in decanting into the transmission tubes. It was found best to allow these tubes to stand about two hours before taking observations. Many air bubbles then collect at the top of the tube where they do not effect the transmitted beam. In some cases all bubbles are not gone in a day's standing, but generally after two hours it was assumed that the two tubes were near enough in the same condition to warrant observations. Four hours would give the same results, whereas a day's standing might show either turbidity or a precipitate, and, at least, irregularities.

## III. THE COPPER SOLUTIONS.

The copper salts all have a common absorption band in the red (Fig. 2), which would give them in solution a dark blue color. Copper chloride, in a strong solution, absorbs also in the blue, which leaves this solution green. According to the Ostwald theory,[2] we may then look for ionic absorption in the common band. This result is exceptionally well verified in the red absorption region, where upon dilution the absorption in the nitrate, sulphate and chloride are practically identical both in position and magnitude. But it is also clear that this absorption region is not due to the ions alone in the solution in general; for then the region would grow relatively darker upon dilution. The opposite effect takes place in the nitrate and chloride. There is no change in the sulphate. This indicates that in whatever region there is ionic absorption there is also molecular absorption, and it is clear that the molecular absorption is greater than the ionic in the nitrate and chloride, and equal to it in copper sulphate salt. The chloride and nitrate molecule absorb more than the copper sulphate molecule. In the dilutions here studied dissociation is far from complete; so that some difference in the absorption region is expected, even in dilute solution. Since there is considerable difference in the molecular absorption, more difference should have been expected in solutions of the present dilution than was observed. This appears, however, within the limits of error. The action of the acid is apparent. For the chloride and nitrate it has more than restored the dilute solutions to their original condition; *i. e.*, it has repressed the ions to the molecular condition, and shows that relatively there are more molecules in solution than in the concentrated form. The acid makes no difference in the copper sulphate ion; that is, there seems to be no essential difference between the ion and the molecule of this salt.

### Table III.

½$Cu(NO_3)_2$.

| ½$Cu(NO_3)_2$ | 6.209<br>7.169 | 2.576<br>2.804 | .0787 | .0787 |
|---|---|---|---|---|
| $HNO_3$ | 0 | 0 | 0 | 13.72 |
| λ | *A* | *A* | | |
| 690.0 | 2.67 | 3.67 | 3.70 | 2.37 |
| 669.0 | 3.63 | 4.54 | 5.59 | 3.73 |
| 650.0 | 5.12 | 6.34 | 7.07 | 4.92 |
| 632.5 | 6.78 | 8.40 | 9.52 | 6.83 |
| 616.5 | 9.11 | 11.9 | 13.46 | 10.48 |
| 602.5 | 14.1 | 16.9 | 19.2 | 14.4 |
| 589.6 | 21.8 | 28.3 | 27.6 | 21.6 |
| 577.0 | — | | 38.4 | 31.35 |
| 564.5 | 40.1 | | 53.6 | 43.56 |
| 553.5 | — | | 69.5 | 61.3 |
| 543.5 | 80.9 | | 94 | 84.5 |
| 534.0 | — | | 135 | 120.5 |
| 525.0 | 150.5 | | 180 | 168.6 |
| 517.0 | — | | 247 | 232.4 |
| 509.0 | 316.4 | | 330 | 307.6 |
| 501.5 | | | 371 | 360.4 |
| 494.0 | 597 | | — | 490 |
| 479.5 | 818.5 | | 392 | 728 |
| 468.0 | — | | — | — |
| 456.0 | 913 | | 450 | 993 |
| 446.0 | — | | — | — |
| 436.0 | 913 | | 666 | 1201 |

Were we to regard the results with acid in the nitrate and chloride as a condition of approximately no ions, and from the electrical data estimate the degree of dissociation in dilute solutions, or even assuming the value here found for copper, compute the ionic absorption, we have a means at hand for calculation of the absorption for different concentrations, or for the calculation of the degree of dissociation of various concentrations. When, as before mentioned, the required accuracy in optical measurements is obtainable, this quantitative method will be justifiable. The present data do not reach this limit of sensibility, but the results show the possibility of the application. Dissolving the substance in an organic solvent, where the dissociation is minute, and calculating the molecular absorption from it and applying these values to water solutions, is a questionable process. This method rests upon the assumption that a substance, so long as its chemical nature is unchanged, has the same absorption in different solvents. This is contrary to Kundt's law,[8] which has generally been confirmed by various experimenters. Vaillant[6] does get almost identical values for the absorption of copper sulphate in alcohol and glycerine at three points (very close together) in the spectrum. This is too fragile a basis to conclude that it has the same color in all organic solvents, or that concentrated water solutions tend toward the limit of organic solutions, or that the undissociated molecules in water have the same absorption as in organic solutions. Ley[24] points out that copper chloride in alcohol is a pure green, in aceton a yellow green, in urethan yellow, in pyridin blue. In all of these the dissociation is small.

When we consider the part of the spectrum where the absorption is small (see Fig. 2) the data are not so readily interpreted. The dilute solution curve of the nitrate differs considerably from the sulphate and chloride. The sulphate and nitrate are much more transparent when acid is added. The same treatment causes the chloride to darken. The nitrate is the most transparent and its curve crosses the sulphate. The concentrated chloride is nearly black in this region, but upon dilution reaches a value almost identical with the sulphate. In the nitrate the action is the opposite and darkens upon dilution. The sulphate again shows no appreciable change upon dilution. The incomplete dissociation of the nitrate molecule is a reasonable explanation of the difference between its dilute solution curve and the one for the sulphate. On the other hand, the dark chloride is as transparent as the sulphate and it must have still considerable quantity of the undissociated molecules present. As seen later in this paper, there is a possibility of attributing this entire dark band to another product in solution, which disappears upon dilution; so that the real copper chloride molecule may be as transparent as the sulphate, and the absorption upon dilution could be as observed. In great dilution the absorption of the nitrate, sulphate and chloride are probably also identical in this region. This gives complete identity throughout the spectrum.

Table IV.

½($CuCl_2$).

| ½($CuCl_2$)<br>HCl<br>λ | 6.8g<br>0<br>A | .068g<br>0<br>A | .068g<br>4.5<br>A |
|---|---|---|---|
| 690.0 | 2.15 | 3.92 | 2.02 |
| 669.0 | 3.47 | 4.67 | 2.63 |
| 650.0 | 4.51 | 6.91 | 3.96 |
| 632.5 | 6.45 | 9.73 | 5.54 |
| 616.5 | 9.11 | 13.6 | 8.63 |
| 602.5 | 12.65 | 20.7 | 11.7 |
| 589.6 | 19.67 | 29.1 | 18.2 |
| 577.6 | — | 36.7 | 29.1 |
| 564.5 | 52.5 | 60.9 | 37.5 |
| 553.8 | — | — | 46.3 |
| 543.5 | 106.5 | 115.2 | 64.4 |
| 534.0 |  | — | 79.9 |
| 525.0 | 156. | 180.1 | 61.6 |
| 517.0 |  | — | 55.2 |
| 509.0 | 133.7 | 270.2 | 45.4 |
| 501.5 |  |  | 32.5 |
| 494.0 | 68.4 |  | 18.8 |
| 487.0 |  |  | 12.9 |
| 479.5 | 33.4 | 287.6 | 7.5 |
| 474.0 | 22 |  | 5.4 |
| 468.0 | 17.1 |  | 4.2 |
| 456.0 | 8.8 | 238.2 |  |
| 436.0 |  | (221.3) |  |

The copper acetate forms a series of values not to be compared with the other data. It is much darker than the nitrate and the sulphate. It has necessarily small dissociation which might appear as a reason for finding no difference between the concentrated, dilute and acid solutions in the band region. But the position of the curves suggest widely different values between molecular and ionic absorption, so that a difference should exist. In the more transparent region there is an action similar to that observed in the nitrate and sulphate, *viz.*, a darkening upon dilution and a clearing upon adding acid. Müller studied copper acetate in molecular concentrations of .111 and .006. He discovered a marked change upon dilution. His values are all radically different from mine, which suggests that the difference lies, possibly, in the presence of other products in my solutions. The copper acetate was a commercial product and in solution may have contained basic acetate. Vaillant's[6] observations cover three points within the band of copper acetate. He observed double transparency upon dilution and a darkening of nearly four fold upon adding acid.

It is well to examine these solutions from the standpoint of Hartley.[8] The copper sulphate $CuSO_4.5H_2O$ and $Cu(NO_3)_2.3H_2O$ have weights of about the same magnitude, and, consequently little difference in the bands. $CuCl_2.2H_2O$ is thirty per cent. lighter. It should, therefore, vibrate more freely. What acually occurs is, the red absorption band retains the same identical position as the other coppers. Instead of being displaced toward the shorter wavelengths it further absorbs more than either of the other two salts. Beside, there is an added band in the blue and violet.

The theory of Jones and collaborators upon hydrates in solution has little in common with the older hydrate theory. We may best quote from a recent paper:[18] "The theory of hydrates in aqueous solutions is to be sharply distinguished from the old hydrate theory of Mendeléeff which having long since been shown to be untenable, has been abandoned. According to the older theory when a substance like calcium chloride is dissolved in water there are formed certain definite compounds with perfectly definite amounts of water." According to the new theory "the compounds formed are at best very unstable and vary in combination all the way from one molecule to a very great number." . . . "Thus the composition of the hydrates formed by calcium chloride may vary all the way from a few molecules of water up to at least thirty molecules and may have all intermediate compositions depending solely upon the concentrations, temperature being, of course, understood to be constant."

The data of Jones show, generally, relatively more hydrates in dilute solution, and if the molecules and ions are intimately enough associated with the water to effect the freezing point as a whole, we may expect such combinations to show characteristic periodic vibrations, and, therefore, characteristic absorption. For example, in the dilute solutions containing relatively large amount of water, the total weight of the molecule would not change appreciably by changing one of the ions, and in dilute solutions the salts containing a common ion, would have practically identical absorption. However, the concentrated solutions having relatively less water in combination, would vibrate more rapidly and give shorter wave-length absorption. That is, there would be a shift of the band from blue toward the red upon dilution. This may be illustrated by data taken from a recent contribution by Jones and Bassett[18] which appeared about the time of the suspension of the observations. For a copper sulphate solution of a concentration of .1301 gram molecules they find 27.1 molecules of water associated with each copper molecule; and for a concentration of copper sulphate solution of 4.371 gram molecules 11.4 molecules of water associated with each copper molecule. These hypothetical additions of water molecules are associated intimately enough with the copper to reduce the effective water in the solution, and hence give the equivalent of abnormal concentrations in solution and, therefore, abnormal lowering of the freezing point. The entire molecule in dilute solution is about 1.54 times its weight in the concentrated solution without making any assumptions as to the damping action of a viscous medium or as to the shape of the molecule and assuming inertia proportional to the mass, the period of vibration would be about 2.3 times as long. Beginning, therefore, with an absortion band in the spectrum for a concentrated solution, one would then have upon progressive dilution a band shifting toward the red and ultimately passing entirely out of the spectrum. No such phenomenon is observed in these experiments, and, in fact, if it existed at all, would have long ago been a well-known phenomenon to the unaided eye. The actual conditions are probably such as to leave this an exaggerated illustration, but granting this, one still feels compelled to state that there can be no intimacy of association between the hydrate water and the salt without a displacement of the band, and it appears remarkable that the water is still intimately enough associated to effect the freezing point values.

Hence, so far as the absorption spectrum is concerned, the molecules must be vibrating in their own little sea of associated water much the same as the non-hydrates in any water solution. A salt which forms a hydrate when added to a solution containing a colored solute, may also affect the color and remains to be considered.

TABLE V.

$\frac{1}{2}Cu(C_2H_3O_2)_2$.

| $\frac{1}{2}Cu(C_2H_3O_2)_2$ $HC_2H_3O_2$ $\lambda$ | 0.684 0 $A$ | 0.0342 0 $A$ | 0.0342 $x$ $A$ |
|---|---|---|---|
| 690.0 | 1.46 | (1.55) | (1.40) |
| 669.0 | 1.60 | (1.63) | (1.56) |
| 650.0 | 1.92 | (1.95) | (1.90) |
| 632.5 | 2.50 | (2.65) | (2.49) |
| 616.5 | 3.50 | (3.60) | (3.45) |
| 602.5 | 5.1 | (5.33) | (5.15) |
| 589.6 | 7.6 | 8.15 | 7.69 |
| 564.5 | (16.4) | 16.54 | 15.75 |
| 543.5 | (32.0) | 31.8 | 30.45 |
| 525.0 | (53.1) | 52.7 | 50.6 |
| 509.0 | (80.7) | 81.4 | 86.0 |
| 494.0 | — | — | |
| 479.5 | (104) | 97.7 | 111.2 |
| 468.0 | | — | |
| 456.0 | (95) | 82.8 | 116.8 |
| 436.0 | (74) | 62.9 | 109 |

Such a hydrate salt practically increases the concentration of the original salt, and if the latter is colored, its character of absorption would be the same as another solution of increased concentration with other proportions of hydrate water and another degree of dissociation. For example, if the new salt required 90 per cent. of the water present for its hydrate, then there remains to the original components 10 per cent. of the water. This involves a change in the dissociation of the latter, corresponding to a change in concentration. Consequently, there is a change in color if there was a change upon dilution. This is also what would follow from the law of mass action in solutions containing common ions. This process does not involve, however, unless present by reason of the above action, any general change in intensity or color, because if, in the above illustration, there only remains to the colored salt one tenth of the original water, there remains, also, if absorption is an additive property of the components only, but the equivalent of one tenth of the length. The only question then is whether the repression of the ionization is proportional to the dissociation, *i. e.*, to the free ions of the added salts, or whether it is proportional to the equivalent increased concentration arising from the hydrated salt added. The free ions added can advantageously be those formed from a hydrate which has no ions common to the colored ion. Lewis[19] observed such changes of tint with his colorimeter, which suggests changes proportional to the added hydrates. The phenomenon needs a careful comparison of the conductivity, freezing point and spectrophotometric data.

The copper chloride, which possesses two absorption regions, is here studied only in concentrated and in dilute solutions, but Müller has studied the salt in intermediate concentrations. In this salt there is a rapid change in the blue region out of all proportion to the ionization. These changes cannot be attributed to the hydrate, inasmuch as there is, firstly, no displacement of the band. Secondly, in the red absorption region, the changes are uniform and what might be expected in a change from the molecular to the ionic condition. The irregular changes in band should have been present here also, if found in the other band, for two reasons: Firstly, not all the red band can be attributed to the ions; and, secondly, the new hydrates are supposed also to be associated with the ions, and the total weight of a hydrate does not change much, in a change from the molecular to the ionic form. If the new hydrate possesses no characteristic absorption of its own, there is still an equivalent change in concentration which, likewise, affects the entire spectrum. Therefore, even if the red absorption were due to the ions alone there should be important changes throughout the spectrum out of proportion to the rate of ionization, instead of only in the blue absorption. So that the changes in the blue absorption indicate the presence of another product instead of a hydrate. The investigation of Ley[24] suggested to him that the change from blue to green upon heating dilute copper chloride was a change from

$CuCl_2 \rightleftarrows Cu^{\cdot\cdot} + 2Cl'$ to
$CuCl_2 \rightleftarrows CuCl^{\cdot} + Cl'$.

Inasmuch as an increase in temperature is similar in its color effect to an increase in concentration, it is possible that the blue absorption of the concentrated solutions arises from the CuCl, which disappears upon dilution. A similar phenomenon will be later noted in cobalt chloride. Vaillant[6] observes changes in some copper solutions, particularly the bromide, which are out of proportion to the absorption coefficients. His principle readings are in the red band, *i. e.*, the ionic band. If these readings were extended to the whole spectrum they might show the same discrepancy throughout, which would be an indication of the new hydrate.

TABLE VI.

$\frac{1}{2}Co(NO_3)_2$.

| $\frac{1}{2}Co(NO_3)_2$ $HNO_3$ $\lambda$ | 5.45 0 *A* | .0545 0 *A* | .0545 13.72 *A* |
|---|---|---|---|
| 690.0 | 66.9 | 84.1 | 69.3 |
| 669.0 | 51.4 | 66.6 | 55.9 |
| 650.0 | 40.9 | 57.8 | 46.1 |
| 632.5 | 35.5 | 54.8 | 44.9 |
| 616.5 | 32.2 | 51.1 | 43.5 |
| 602.5 | 29.4 | 48.7 | 38.4 |
| 589.6 | 26.0 | 41.5 | 30.5 |
| 577.0 | 20.7 | 30.6 | 20.4 |
| 564.5 | 12.4 | 19.5 | 12.4 |
| 553.5 | — | — | |
| 543.5 | 5.56 | 6.96 | 5.15 |
| 534.0 | — | — | |
| 525.0 | 3.40 | 4.64 | 3.35 |
| 517.0 | — | — | |
| 509.0 | 3.19 | 4.49 | 3.04 |
| 479.5 | 4.23 | 5.51 | 4.40 |
| 456.0 | 4.95 | 7.39 | 5.56 |

Graham introduces a classification of hydrates (referring to crystals), calling some of the water molecules water of constitution and other molecules water of crystallization.[22] The only distinction he makes between the two kinds of molecules is that the water of constitution is not supposed to effect the color. Could the new unstable hydrates fall into this class? MacGregor[23] discusses theoretically the variations of water solutions of salts with temperature and concentration from the standpoint of the gas theory. He concludes that there are a number of molecules of water grouped around (probably not in) the salt molecule and form a complex whole, which he calls a physical hydrate to distinguish it from a chemical hydrate. He notes that an increase of temperature or of concentration decreases the amount of water grouped with the molecule, which, in a measure, predicts the results of Jones. He also states that an increase in temperature will have the same effect upon absorption as an increase in concentration when the concentration is moderate, but will have an opposite effect to change in concentration when the latter is very great. I interpret this to mean that the temperature coefficient changes sign at a certain concentration. Such a test would be interesting, but would not be so very conclusive if it was verified. According to this theory, MacGregor states that the water exercises no particular absorption on account of its transparency. The absorption is to be attributed to the molecular hydrates of the salts or to the dissociation products.

## IV. The Cobalt Solutions.

The spectrum of the water solutions of cobalt have a common absorption band beginning between the *C* and *D* Fraunhofer lines, and extending as far as examined nearly to the *G* Fraunhofer line. The maximum absorption is located about 525 $\lambda$. The dilute solution of the sulphate, nitrate and chloride, are not as near equal in this band as was observed for the corresponding copper salts in their common band. Still they are near enough to indicate their equality with reasonable certainty for identical concentration in solutions of greater dilution. From the *C* line toward the red limits of the spectrum, the nitrate shows rapidly increasing transparency. The sulphate shows another absorption band in the red with maximum absorption poorly defined and increasing in transparency toward the red limits and transparency possibly as great as the nitrate. The absorption of the chloride in the red is so large as to leave a small transmission band in the orange, which suggests two overlapping absorption bands. Beside the broad red band, there are two well defined sharp bands nearly as narrow as lines in the dark red. These lines or bands are too narrow to indicate their presence in spectrophotometric observations, but the author has not observed lines between *G* and *F*. A prominent feature of the process of dilution is the rapid diminution of this band in the sulphate and chloride, *i. e.*, the product which causes this absorption is rapidly disappearing, and with great dilution there might be expected an identical curve throughout this part of the spectrum as well as in the common band region. The molecular absorption in the band region is greater than the ionic. The chloride shows the greatest difference between molecule and ions, the nitrate next and sulphate least. This is the order in the copper salt solution, except in the latter the sulphate difference is zero or nearly so. Dilution in the salts increases transparency in all parts of the spectrum. The action of nitric acid in depressing the ionization is marked. One, however, should have anticipated greater effect.

The action of hydrochloric acid upon the chloride was more apparent, but slight differences in the concentration of the acid changed the transmission coefficient appreciably. A trial of the effect of sulphuric acid upon cobalt sulphate gave increased transparency. It was thought that this action was due to slight precipitation, and this surmise was later verified. The color changes of cobalt chloride upon dilution and the changes attending the mixture of cobalt chloride with salts and with hydrochloric acid are well known and have recently been the subject of renewed discussion by Hartley[3] and Donnan and Bassett[20] and more recently by Lewis.[19]

Hartley[3] examined hot and cold solutions of cobalt chloride and regards the phenomenon as explanable upon the "old hydrate" theory, and Lewis[19] contends for the "new hydrate" theory. The latter fails to discuss the previous observations of Donnan and Bassett,[20] whose method leaves scarcely a doubt of another product in solution, which would give the action noted by Lewis. Donnan and Bassett always used concentrated cobalt chloride in their mixtures. Their method is an electrical one and establishes the presence of a complex anion of cobalt in these solutions. The method causes the cobalt to migrate against the current, from a mixture of cobalt chloride in hydrochloric acid, into a hydrochloric acid solution. A blue color is formed similar to the blue of the mixed solution. They compare the color with cobalt chloride in water solution and conclude the product also present in the solutions of Hartley. No photometric measurements are made, and just here Hartley had noted a difference in colored acid solution and colored hot-water solutions. This fact leads Hartley to comment "that to compare mere similarities of color is a less precise method of examination than that of observing absorption spectra through varying thicknesses of solution, and can give but little evidence of chemical constitution unless the color is very marked and practically identical with those already known and capable of identification by their color." This is not valid for indication and proof that a complex colored ion is present in solution. Because if cobalt migrates against the current it is carried as a complex anion. Recognizing this, Hartley admits a possible complex ion in their solution, stating "that Faraday had shown that when fused stannous chloride was electrolysed, stannic passed to the anode, and stannous to the cathode." He further adds that the spectra of the various solutions of cobalt chloride at 23° C., 33° C., 43° C., 53° C., 73° C. and 93° C. are none identical with the anhydrous cobalt chloride dissolved in hydrochloric acid or in alcohol. This same class of hydrates is assumed in the work of Vaillant.[6] If the complex product noted by Donnan and Bassett was present in their experiments, its presence will explain the action noted by Vaillant. As will be seen later, the color of cobalt solutions depends almost entirely upon the concentration of acid at least as long as the cobalt is dilute. Consequently to add cobalt in small quantities directly or through action of an electric current would give blue color, the tint depending upon amount of acid and intensity upon amount of cobalt, and a spectrophotometric examination could tell only what the unaided eye can infer, *viz.*, that cobalt is present, but in what form is a matter of inference from its anionic character. It is perhaps well also to note in this connection concerning the discussions of both Donnan and Bassett, and of Hartley, and of the work of Vaillant,[6] that it is possible to emphasize too much an identity or lack of identity of the absorption of a substance in different solvents. Kundt's law[8] requires a displacement of the absorption band upon change of solvent. Experiments have shown such changes, but sometimes in the direction opposite to the requirements of the law. It is not permissible to say that a hot cobalt chloride solution in water has the same composition as an anhydrous cobalt chloride solution in alcohol or hydrochloric acid, even if the absorption should prove identical. Likewise their non-identity is not proven by a different absorption. It may be questioned whether a difference like that between Hartley's absorption of cobalt chloride in hydrochloric acid and in water at 93° C. is not of a character which arises from a change of solvent only. Hartley only gives a curve for one concentration of hydrochloric acid, and notes that the color of the cobalt solution does not change upon adding more hydrochloric acid. Just how he makes this change is uncertain. If he means that by adding hydrochloric acid without changing its concentration in solution with respect to water, I have verified it. But this is in reality only a change in the concentration of the cobalt chloride. But if there is a change in the concentration of the acid with respect to the water the changes later noted in this paper are enormous and show that color depends upon the concentration of the acid only, and remind one very much in their character of changes upon heating the water solutions, where color depends principally upon the temperature. As noted, a general similarity or considerable difference will not unqualifiedly prove or disprove a difference of composition. The evidence to the author's mind is at least suggestive of a similar process, in the acid and water solutions, and a product as indicated by Donnan and Bassett.[20]

The increase in transparency of the cobalt chloride in the red upon dilution, as shown by the recorded readings in Table VII., and by two observations (not repeated) for two intermediate concentrations, shows changes out of proportion to the change from molecular to the ionic condition, as noted in the copper chloride studied by Müller.[16] Lewis[19] would attribute this to hydrates, which is a rather improbable supposition. One may as readily assume that there are here complex ions which disappear rapidly upon dilution. This would be in keeping with the observations of Donnan and Bassett. Such a complex ion is also suggested by the observations of Bien[21] upon the transport numbers of cobalt chloride. He found a transport number for a .1 per cent. solution of

## TABLE VII.

½ $COCl_2$.

| ½$COCl_2$<br>Added Component. | 6.80<br>0 | .034<br>0 | ½ ($ZnCl_2$)<br>.017<br>5.95 | ½ ($ZnCl_2$)<br>.017<br>10.6 | NaCl<br>.017<br>.545 | NaCl<br>.017<br>5.45 | $NH_4Cl$<br>.017<br>.524 | $NH_4Cl$<br>.017<br>5.24 | HCl<br>.0068<br>.034<br>4.96 | HCl<br>.0034<br>.017<br>5.75 | HCl<br>.0034<br>.017<br>6.51 | HCl<br>.0034<br>.017<br>7.12 | HCl<br>.0034<br>.017<br>8.74 | HCl<br>.0034<br>.0068<br>10.8 | HCl<br>.0034<br>12.1 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| λ | *A* | *A* | *A* | *A* | *A* | *A* | *A* | *A* | *A* | *A* | *A* | *A* | *A* | *A* | *A* |
| 713.5 | 8.91 | 49.5 | — | — | — | — | — | — | | | | | | | |
| 690.0 | 6.61 | 43.9 | 29.2 | 27.0 | 36.6 | 26.7 | 39.5 | 23.8 | 30.7 | — | — | — | | | |
| 669.0 | 6.72 | 40.4 | 26.3 | 23.8 | 33.3 | 24.1 | 36.4 | 20.5 | 24.8 | 4.74 | .99 | — | | | |
| 650.0 | 7.93 | 39.4 | 25.8 | 22.8 | 33.0 | 23.7 | 35.1 | 20.2 | 24.5 | 4.52 | .96 | — | | | |
| 632.5 | 8.36 | 42.5 | 26.7 | 23.7 | 36.0 | 25.1 | 37.3 | 22.7 | 25.2 | 4.88 | 1.20 | — | | | |
| 616.5 | 9.32 | 45.7 | 28.2 | 24.7 | 40.8 | 27.2 | 40.4 | 25.0 | 28.7 | 6.20 | 1.35 | .594 | | | |
| 602.5 | 10.40 | 47.6 | 29.7 | 25.5 | 43.0 | 29.2 | 44.0 | 25.9 | 31.6 | 6.85 | 1.63 | .664 | | | |
| 589.6 | 9.63 | 43.4 | 24.7 | 21.5 | 36.5 | 22.3 | 37.8 | 21.2 | 35.9 | 8.53 | 2.39 | 1.16 | .395 | .378 | (.368) |
| 577.0 | 7.21 | 31.4 | 19.5 | 15.5 | 28.0 | 16.1 | 27.3 | 14.7 | 35.4 | 10.1 | 4.09 | 2.47 | .817 | .527 | (.414) |
| 564.5 | 5.10 | 19.65 | 13.4 | 10.5 | 19.0 | 9.64 | 19.1 | 9.12 | 26.7 | 9.26 | 5.57 | 3.39 | 1.55 | .85 | (.738) |
| 553.5 | 3.86 | 12.56 | 96.3 | 8.15 | 12.4 | 7.86 | 12.5 | 6.36 | 17.7 | 7.27 | 4.58 | 3.46 | 2.42 | 1.86 | (1.62) |
| 543.5 | 3.06 | 8.40 | 6.71 | 5.69 | 6.98 | 4.99 | 7.07 | 4.79 | 9.86 | 5.72 | 3.73 | 3.15 | 2.59 | 2.51 | (2.40) |
| 534.0 | — | — | 5.43 | 4.48 | 6.16 | 4.10 | 6.26 | 4.00 | 5.75 | 4.07 | 3.13 | 2.76 | 2.50 | 2.45 | (2.40) |
| 525.0 | 2.39 | 5.01 | 4.58 | 4.09 | 5.25 | 3.68 | 5.38 | 3.63 | — | 2.85 | 2.57 | 2.47 | 2.25 | 2.37 | (2.30) |
| 517.0 | — | — | 4.25 | 3.93 | 4.81 | 3.63 | 4.98 | 3.69 | 3.62 | 2.85 | 2.45 | 2.34 | 2.26 | 2.29 | (2.25) |
| 509.0 | 2.40 | 4.82 | 4.28 | 4.00 | 4.85 | 3.79 | 5.02 | 3.77 | — | 2.85 | 2.50 | 2.50 | 2.60 | 2.74 | (2.80) |
| 501.5 | — | — | 4.49 | 4.23 | 5.01 | 4.04 | 5.19 | 3.95 | 3.55 | 2.90 | 2.73 | 2.69 | 2.95 | 3.30 | (3.65) |
| 414.0 | — | — | 4.98 | 4.76 | 5.33 | 4.43 | 5.36 | 4.37 | — | 3.05 | 3.12 | 3.00 | 3.40 | 3.81 | (4.2) |
| 479.5 | 3.07 | 6.15 | — | — | 6.10 | 5.80 | 6.32 | 5.17 | — | 3.32 | 3.49 | 3.47 | 4.30 | 4.65 | (5.15) |
| 456.0 | 4.77 | 7.82 | | | | | | | 4.58 | 4.10 | 4.31 | 4.26 | 5.07 | 6.21 | (6.95) |
| 436.0 | 7.73 | | | | | | | | 5.66 | | | | | | |

cobalt chloride at 18 of .404 for cobalt. When this concentration was 49 times as great and the temperature 27° C., the transport number was reduced to .264. This is readily explained by the presence of a complex anion of cobalt, in the stronger solutions migrating against the current.

When the mixed solutions of cobalt chloride, with sodium chloride, ammonium chloride, and zinc chloride are compared with the cobalt chloride diluted in water only, a marked repression of the dissociation is noted. This seems to be in all cases much less than should have been anticipated by the law of mass action. The more dilute sodium chloride solution contained about 31 times as much chloride as the cobalt. However it is the quantity of anions that determines the repression of the dissociation. The sodium chloride is less dissociated than the cobalt and the ratio for the corresponding ions falls much below 31. Fach of the salts of sodium and ammonium chloride was tested in two concentrations — the stronger ten times the weaker. In the weaker solutions the sodium chloride depresses the dissociation more than the ammonium chloride. In the stronger solution the phenomenon is reversed. This apparent anomaly was explained when a comparison of the electrical conductivities of these salts was made. In the weaker solution sodium chloride is nearly twice as good a conductor as ammonium chloride. In the more concentrated solution the conductivity of the ammonium chloride is over 1.8 times that of the sodium chloride. The zinc chloride also shows depression of the dissociation, but less for the same concentration than the other salts. Donnan and Bassett[20] state that "red aqueous solutions (of cobalt chloride) may be turned blue by the addition of chlorides of metals of pronounced basic function, chlorides of magnesium and calcium are very effective." . . . "Chlorides of potassium and sodium appear to be not so effective. Chlorides of zinc, mercury, antimony, tin, etc., act in opposite manner, *i. e.*, if added in sufficient quantities turn blue solutions, red, whether the blue solution is obtained by increased temperature or by added salt." The observations here recorded indicate the opposite action of zinc chloride. Donnan and Bassett[20] were, however, dealing with concentrated cobalt chloride. They explain this phenomenon on the assumption of a complex ion of the form $MB_3''$

or $MB_4''$ for these bivalent metals transparent for all of them except cobalt chloride; and it having strong absorption in the red. The normal ion is then supposed nominally transparent in this region. Supposing that to $M^{\cdot\cdot}$-$MB_3''$ colored, is added $M^{\cdot\cdot}$, $MB_3''$ transparent, in such a way as to increase quantity of negative ion. The equations for mass action requires that $MB_3''$ colored diminish, *i. e.*, in this case the solution becomes red. Whereas if to $M^{\cdot\cdot}$, $B''$ dilute, is added another component containing $M^{\cdot\cdot}$, $B''$ and some reaction takes place between the latter component and dilute solution. Some of the MB molecule is formed; and from the MB molecule, there will be produced some $M^{\cdot\cdot}$-$MB_3''$. In the case of the chloride of cobalt this product has absorption in the red. In this case then the cobalt solution becomes less transparent in the red as in the above observations. For the observations with the present added salts taken alone, there is no need of any assumption of more than simple ions. If the color changes produced by these salts arose from the hydrates of Jones and Bassett,[18] the greatest change should have been produced by the zinc chloride instead of the least as observed. The same statement holds for the added sulphate salts.

The addition of these salts never sufficed to restore the partially dissociated cobalt solution to the condition of the concentrated solution. When mixtures of hydrochloric acid and cobalt chloride, however, were studied, it became apparent that the original condition was restored when about 5 equivalent of the acid was used. Further addition of acid did not bring the data to the ultimate limit of ions restored to the form of cobalt chloride molecules, but caused more marked changes than ever. Every addition of acid increased the absorption in the red and transparency in the violet. This indicates a new product and possibly a product also present in considerable proportions in the original concentrated solution, and possibly the complex ion indicated above. It may also mean a change in solvent. It may mean both of the changes combined. It was found that the absorption did not depend upon the concentration of the dilute cobalt solution but upon the concentration of the acid, *e. g.*, maintaining the acid constant and varying the concentration of the cobalt five fold did not affect the absorption. This fact would generally be fatal to the complex anion hypothesis. But when we consider that the smallest ratio of hydrochloric acid to cobalt chloride is three hundred, the transformed portions might in all solutions be so near equal that no difference could be detected. However, a change in the acid of a small percentage produced a marked effect upon the color. For example in a solution containing $x\mathrm{C_0Cl_2}$, $y\mathrm{HCl}$, and $z\mathrm{H_2O}$, where $x$ is small, a variation of $x$, five fold, gives identical equivalent transmission coefficients. A change of a few per cent. of $y$, and $x$ varying as before, gives another set of coefficients all falling upon another curve. If it is a question of mass action, this difference should not have been noted, as the ratios of $x$ to $y$ in the two sets of readings are in some cases identical. The phenomenon is, however, explicable upon the hypothesis of a change in the solvent from water to hydrochloric acid. Suppose a substance $A$, soluble in $B$ and also in $C$, and nothing whatever said as to the form of the $A$ product in $B$ or in $C$. Let the $A$-$B$ mixture be red and the $A$-$C$ mixture blue, so that their transmission curves form a cross like the letter X. Their transmission curves then intersect at some point in the spectrum. If parts of $A$-$B$ and of $A$-$C$ be placed in the path of the light a transmission curve will be obtained intermediate between the two and intersecting at their common intersection. The curve will be nearer to $A$-$B$ or $A$-$C$, according to which is used in greater quantities. This will not effect the transmission coefficient through all ranges of values for $A$ under saturation and constancy of the product $A$. Neither will it be affected if $A$ takes the form $A$-$B$, *e. g.*, simple ion, molecule or hydrate, and $A$-$C$, *e. g.*, complex ion or complex molecule. All the curves, after 6.5 equivalents of hydrochloric acid are added, which one may regard as having removed dissociation, are included between two such extremes, and as nearly as could be expected intersect in a common point. The actual intersections lie between 525 $\mu\mu$ and 515 $\mu\mu$. The writer fails to see wherein the argument is invalidated if the solvents, hydrochloric acid and water are miscible in all proportions.

In the study of cobalt sulphate the addition of $\mathrm{ZnSO_4}$ caused an increase in transparency. There was a suspicion of slight precipitation in the solution as there had been in the case of cobalt sulphate, sulphuric acid solutions. It was thought that this could possibly arise from the total concentration of $SO_4''$, exceeding the saturation value for cobalt sulphate. The concentration was therefore taken below this limit. The result is given under $\frac{1}{2}(ZnSO_4)$ of concentration 4.742, Table VIII. This gives a diminution of the section, but increased transparency is still present. Since this action extended through the spectrum (blue readings are marked uncertain and not recorded) and not limited to one color, the writer still clung to the idea of a slight precipitate. The zinc sulphate was accordingly reduced to .114 equivalent and another test made. This concentration yielded results similar to results in cobalt chloride and mixed salts. This result is, however, much less pronounced. However, this was to be expected, as the cobalt sulphate changes upon dilution are much smaller than those of the chloride. It was not so difficult to prove the formation of a precipitate in the sulphuric acid solutions. By increasing the acid strength the precipitate was soon marked enough in the bottom of a beaker to recognize. Another phenomenon is worthy of notice. If strong sulphuric acid is added to a moderately concentrated water solution of cobalt sulphate, a precipitate soon forms which is redissolved upon further addition of acid. The deep red color is characteristic of the latter solution. The writer wasted 70 per cent of his observations upon this mixture before he fixed the inconsistencies of obervations upon this kind of a change in the dilute solutions of cobalt. He had thought the difficulty in the diffuse radiation (before mentioned) to arise from small air bubbles in the acid, a difficulty always present, and hiding the serious difficulty by the diffusion. The precipitate in suspension even in minute quantities darkened the whole field, but more especially the red. When precipitated it removed an appreciable portion from solution, giving abnormally high transmissions. When redissolved it had another color. Given these three factors at once, and the shaking which arises from repeated handling of tubes during observations, the possibilities of inconsistency are apparent. The difficulty was solved by further diluting the cobalt sulphate. The concentration used with the zinc sulphate mixture was about the maximum that could be used with a 50 per cent. sulphuric acid solution without complication. For the strongest acid a dilution about five times this is necessary. These statements

## Table VIII.

½ $CoSO_4$.

| ½ $CoSO_4$ Added Component. | | | ½ $ZnSO_4$ | | | ½ $H_2SO_4$ | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 4.85<br>0 | .0485<br>0 | .0485<br>5.69 | .0485<br>4.74 | .0485<br>.114 | .0485<br>12.77 | .0278<br>19 6 | .0243<br>21.3 | .006<br>.012<br>24.6 | .006<br>.012<br>28.6 | .006<br>.018<br>32.2 | .006<br>.012<br>34.83 | .006<br>.012<br>35.42 |
| λ | *A* | *A* | *A* | *A* | *A* | *A* | *A* | *A* | *A* | *A* | *A* | *A* | *A* |
| 713.5 | — | 68.3 | — | — | 56.0 | — | — | — | — | — | — | | |
| 690.0 | 45.6 | 58.0 | 75.9 | 62.1 | 51.0 | (44.1) | 48.9 | (58.0) | | | (78.0) | | |
| 669.0 | 38.9 | 54.6 | 66.3 | 57.4 | 46.4 | 42.3 | 45.1 | — | 67.6 | 69.8 | 76.1 | | |
| 650.0 | 37.9 | 49.3 | 58.3 | 56.5 | 46.8 | 41.5 | 46.5 | 52.6 | 67.6 | 67.2 | 74.0 | | |
| 632.5 | 36.5 | 49.2 | 52.9 | 53.2 | 47.5 | — | 47.4 | — | | 48.0 | 48.8 | (80.0) | 20.0(?) |
| 624.0 | — | — | 53.7 | 53.7 | — | — | — | — | 58.4 | | — | — | 38.8 |
| 616.5 | 39.6 | 50.6 | 55.2 | 54.2 | 47.8 | 42.6 | 49.2 | 46.8 | | 22.8 | 21.9 | 21.0 | 20.7 |
| 609.0 | — | — | — | — | — | — | — | — | — | — | — | — | 13.5 |
| 602.5 | 41.5 | 50.8 | 51.5 | 50.0 | 43.3 | 48.5 | 45.1 | 48.0 | 36.0 | 12.5 | 10.0 | 9.52 | 8.86 |
| 595.5 | — | — | | | — | — | — | — | — | — | 7.32 | — | 6.45 |
| 589.6 | 37.7 | 45.6 | 35.1 | 37.9 | 32.4 | 29.6 | 27.2 | 25.2 | 18.8 | 6.10 | 5.49 | 5.82 | 4.80 |
| 577.0 | 25.3 | 34.0 | 24.5 | — | 20.1 | 19.9 | 19.1 | 10.5 | 9.35 | 4.27 | 3.30 | 3.22 | 3.62 |
| 564.5 | — | 21.0 | — | 19.3 | — | 12.6 | 12.3 | 6.39 | 5.47 | 2.94 | 2.80 | 2.72 | 2.56 |
| 553.5 | — | 12.4 | 12.5 | — | 12.5 | 7.30 | 7.50 | 4.37 | 4.10 | 2.48 | 2.37 | 2.25 | 2.10 |
| 543.5 | 6.91 | 7.86 | 8.8 | 7.64 | — | 5.73 | 5.50 | 3.42 | 3.35 | 2.40 | 2.24 | 2.12 | 2.01 |
| 534.0 | — | — | | | | 4.43 | 4.40 | 2.97 | 3.02 | — | 2.22 | 2.22 | 1.98 |
| 525.0 | 4.43 | 4.90 | | | | 3.82 | 3.80 | 2.83 | 2.80 | 2.38 | 2.27 | 2.38 | 2.18 |
| 517.0 | — | — | | | | — | 3.81 | — | — | — | 2.50 | — | 2.48 |
| 509.0 | 3.90 | 4.62 | | | | 3.71 | 3.88 | 2.88 | 3.13 | 2.99 | 2.95 | 3.18 | 2.78 |
| 494.0 | — | — | | | | 4.15 | 4.92 | 3.46 | 3.92 | 3.33 | — | 4.21 | 3.22 |
| 479.5 | 4.78 | 6.10 | | | | 4.72 | 6.45 | 3.82 | 4.87 | 4.11 | 5.64 | 6.15 | 4.45 |
| 467.5 | — | 7.35 | | | | — | — | — | | 5.12 | — | — | — |
| 456.0 | 6.35 | — | | | | 6.6 | 9.90 | 6.28 | 6.34 | — | 9.04 | — | 7.76 |
| 436.0 | 11.2 | 10.0 | | | | 11.6 | — | 9.63 | 10.1 | — | 10.8 | — | 8.90 |

are not made to imply the limit of solubility of cobalt sulphate in mixtures of sulphuric acid and water, but the limits found necessary for consistency in repeated measurements.

The data ultimately secured, possess some common characteristics with the chloride of cobalt in hydrochloric acid. The acid first represses the ionization, partially or completely. Then further addition causes a marked change in the absorption and shows a shift of the band. The final curve clearly corresponds to a solute in a new solvent. All curves lie between the two extremes. The conditions here do not, however, give a common point of intersection. The absorbent in water has its main absorption in the green, but a minor absorption band appears in the red, with a slight diminution in the orange. The absorbent in sulphuric acid has but one band. It is more intense than the main water absorption band and is shifted toward the yellow with respect to the latter band. The absorption diminishes so rapidly toward the red, that, at about 625 $\mu\mu$ its curve crosses the water absorption nearly at right angles. The point of common intersection is not so well defined as in the case of the cobalt chlorides. Curves No. 10, 11, 12, and 13, Fig. 7, intersect in a region where the slope is very steep. Within the limits of accuracy their common point could be at their intersections with 1, 6 or 7. The two points missing, see Table VIII., for curve 8 are badly needed. This curve may intersect with 7 and 10, 11, 12, and 13. This point would then lie considerably higher than an intersection with a curve of no ionization in a water solution. Naturally this latter curve would lie below 1 rather than above both 1 and 6. By putting the common intersection as low as curve 1, curves 7 and 8 do not represent progressive changes from 1 toward 13. In this region curve 9 is very irregular. Then, although there is a moderately well defined place of intersection it is not so well defined as in the chloride and the complexity suggests the presence of some other components. The data also indicate an intersection of the curves in the blue end of the spectrum, but this, even if true, is not well enough defined to follow with accuracy.

There seem to be indications of such an action present in the mixed solutions of copper bromide in water and in alcohol, and possibly in some other mixtures of Vaillant's investigations.[6] His spectrophotometric measurements are not complete enough to prove it, but are adequate to suggest it. For example, he observes absorption extremes for water and alcoholic solutions and for mixtures of the two solvents in a small portion of the spectrum. These mixtures have intermediate values and hence his assumption that the mixtures give absorption which is determined by the ratio of the absorption of the salts in the two solvents.

## Résumé.

1. The spectrophotometric study of solutions of copper chloride, copper sulfate, copper nitrate and copper acetate has been made in more extended portions of the spectrum and in widely varying concentrations.

2. A spectrophotometric study of cobalt chloride, cobalt sulphate and cobalt nitrate is given in concentrated and in dilute solutions.

3. Beside the ordinary method of treatment, salts and acids are added to repress the ionization.

4. Ostwald's law that dilute solutions containing a common colored ion have a common color, is confirmed.

5. The dynamic law of mass action between ions is clearly confirmed by the diminished association due to added salts and acids which contain a common ion.

6. There has been no evidence gathered showing the presence of hydrates in solution having water added to the molecule and the whole playing the role of a molecule. A hydrate which is a physical aggregate of salt and water and not a molecular combination, may possibly be revealed by a thorough comparison of electrolytic, freezing point, and spectrophotometric data. The latter can be studied as in this paper but must be more complete.

7. There is some evidence (but needing a larger study) of complex anions of cobalt, in cobalt chloride water and acid solutions, with both water and acids acting as solvents. The phenomena in copper chloride may be similar to those in cobalt chloride, and a satisfactory explanation of the changes in the one will probably cover the changes in the other and in similar solutions.

8. The addition of strong acids to cobalt chloride and cobalt sulfate suggests a change of solvent. The character of the data suggests a solute distributed between two solvents, miscible in all pro-

portions, without any assumption as to the phase of the solute. This process seems well-defined in the chloride and has some complications in the sulphate.

9. There is a marked displacement of the absorption band upon a change of the solvent.

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# SPARK POTENTIALS IN LIQUID DIELECTRICS.

By Robert F. Earhart.

An extensive literature exists on spark potentials. This is confined, for the most part, to a study of gaseous dielectrics.

In this paper spark potentials, for small distances, in liquid dielectrics are discussed. Extended experiments on the disruptive strength of various oils, used in the insulation of electrical machinery, have been made by several of the companies engaged in the manufacture of such apparatus. No doubt, much interesting matter, so secured, has not been published by the investigating parties.

In the recent publication, Turner and Hobart on the Insulation of Electrical Machinery, various sections deal with the disruptive strength of oils. For the most part, Mr. C. P. Steinmetz is quoted as authority. In the original paper of Mr. Steinmetz,[1] measurements on the potential required to cause a spark to pass between parallel plates are given. These measurements were made with a periodic P.D., an alternate current transformer being used to obtain the required P.D.

The results obtained by Mr. Steinmetz do not agree with those obtained by MacFarland and Pierce.[2] The last named investigators obtained their P. D. from a Toepler-Holtz machine. They experimented on a large number of oils and are the authorities quoted in the Smithsonian Tables edited by Dr. Thomas Gray. In a discussion of the various results obtained,[3] Dr. MacFarlande points out that the method employed by Mr. Steinmetz in measuring distances, interrupted the continuity of the liquid and explained the discrepancy on that ground. In the Steinmetz experiment, two plane electrodes were separated by a solid dielectric, of known thickness, containing a hole. This aperture contained the oil through which the spark passed. Mr. Steinmetz maintains that values of spark potentials obtained by the use of static machines do not afford data which the electrical engineer can accept. Both agree that the electrostatic potential gradient required to cause the passage of a spark between electrodes is constant, although they do not agree upon the value of this constant.

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[1] Proc. Am. Inst. E. E., 1893, p. 85.

[2] Physical Review, Vol. I., p. 165.

[3] Proc. Am. Inst. E. E., 1893, p. 109.

That this not true for air and other gases has long been known, the potential gradient decreasing with increase in distance. Mr. Steinmetz calls attention to the fact that if the curves showing the relation between potential and distance be plotted, an exterpolation of these for air and the various oils, would give a higher potential gradient for air if the distances were small. His computed value for air, at small distances, gives a gradient of 139 kilovolts per cm. and he calls attention to the fact that this is about the value obtained for red fiber and is higher than for any of the oils on which he operated.

The author has made a series of observations on spark potentials in air and $CO_2$, for extremely short distances.[1] The results for air at atmospheric pressure are shown, for purpose of comparison in Plate II. The values obtained were for P.D.'s from a bank of storage cells. In a later paper,[2] similar and almost identical results were reported as secured from an A.C. source. The interesting part of this curve lies in the peculiar bend occurring at a distance of approximately 3 micra and for a potential of about 350 volts. This indicates a change in the law at this point and the value 350 volts corresponds with what is commonly termed the minimum spark potential of air.

Professor J. J. Thomson[3] explains this turning point on the theory that for potentials less than this critical potential, the discharge is carried by free metal corpuscles projected from the electrodes; that for greater potentials both metal corpuscles and ions of the dielectric are the carriers.

In the present experiment, it is desired to extend spark potential curves over extremely small distances, using liquid dielectrics. The

[1] Phil. Mag., 1900, p. 147.

[2] Physical Review, Vol. 15, p. 163.

[3] Conduction of Electricity through Gases, p. 384.

distances cover a range from .118 mm. to .003 mm. and are thus comparable with previous measurements in air.

## CONDITIONS WHICH AFFECT SPARK POTENTIALS.

In such measurements there are a number of variables which must be taken into consideration. The P.D. required to cause a spark between electrodes depends: (1) Upon the distance separating the electrodes, (2) upon the nature of the intervening medium, (3) upon the pressure, (4) upon the temperature, (5) upon the length of time of application of P.D., (6) upon the shape and size of the electrodes, (7) in case the electrodes are not of the same shape, upon which one is positive, (8) upon whether the intervening medium is ionized by the action of Roentgen rays or other means, (9) upon the material of which the electrodes is composed, (10) upon the strength of the magnetic field in which the discharge occurs.

The foregoing list may not be complete, but sufficient work has been done by various investigators to show that any of these causes may modify the values obtained. Some of these apply only to particular cases. The relation between distances and pressures for gaseous media is embodied in Paschen's law. This is fully discussed by Carr.[1] The fourth consideration, *viz.*, that of temperarure, has never been fully investigated. Turner and Hobart[2] quote a series of measurements showing variations in the disruptive strength of some commercial insulators, due to temperature changes. Oiled linen, for example, was one of the insulators tested. The results show a decrease in the disruptive strength with increase in temperature. It seems probable that temperature effects would cause greater variations in liquid than in gaseous media.

The influence of time of application of the P.D. was first investigated by Warburg and is commonly known as the lag. The size and shape of the electrodes has been studied by Baille and others. The results obtained by a number of investigators are compared and discussed by J. J. Thomson.[3] The effect of polarity of the electrode seems to be most important in the case of a point and plane.

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[1] Proc. Roy. Soc., 1903, p. 374.

[2] Insulation of Electrical Machinery.

[3] Conduction of Electricity Through Gases.

Change of the spark potential due to external ionization of the field appears to be confined to gaseous media and has the effect of diminishing the time of lag.[1] Dr. G. M. Hobbs[2] has investigated the effect of the material composing the electrode on spark potential. He has shown that at the elbow or turn of the potential distance curve in air, that this curve lies parallel to the *X*-axis for a certain distance and that this distance of parallelism depends on the kind of metal used as the electrode. For distances greater than those represented by the bend in the curve the nature of the electrode appears to have no effect.

The effect produced by a magnetic field is most pronounced in gaseous media under small pressures. Precht[3] has investigated the case for atmospheric pressures under certain special conditions.

If periodic P.D.'s are applied, the introduction of capacity and inductance in the circuit containing the spark gap may introduce resonance conditions. This would greatly modify apparent values of the P.D. when measured by the usual method.

## DESCRIPTION OF EXPERIMENT.

In this experiment the variation of spark potential with distance is treated. The dielectrics used were kerosene, paraffin oil, olive oil and a transformer oil purchased on the market. One surface consisted of a circular plate 3.80 cm. across the face; this was ground plane but not polished. The other surface consisted of a ball 2.54 cm. in diameter. Both surfaces were of steel. Changes in atmospheric pressure were regarded as unimportant within the limit of accuracy of the experiment. The temperature conditions were very favorable. The mean temperature was 21° C., with variations of not more than one degree. The apparatus was so constructed that only a small quantity of oil was used at one time. The oil was obtained in sufficient quantity and renewed after each discharge. It is believed that this precaution is unnecessary. This point will be discussed later. For measurements on potential through small distances, it is necessary to measure both distances and potentials accurately. Distances were measured by attaching the plane surface to the movable arm of an interferometer from which it was insulated. The ball was insulated from and suitably mounted on the interferometer bed. The surfaces were then brought in contact and separated. The distance of separation could be determined by the number of light fringes, preferably circular, which crossed the interferometer field during separation of the surfaces. Sodium light was used, and from the known wave-length of the sodium radiation, distances were determined. The arrangement as indicated in Fig. 1 *D* and *D′* indicate the surfaces, *M* the mirror on the carriage of the interferometer. The vessel containing the liquid is designated *V.* The ball and plate were so mounted that fresh portions of the surfaces could be brought into contact after each discharge. The point of contact was determined by a galvanometer and small E.M.F. No difficulty was experienced in securing a positive and definite zero setting. P.D. was measured by means of a Weston A.C. voltmeter, properly calibrated, and reading directly to 120 volts. By means of suitable multipliers, potentials up to 1,500 volts could be measured. The result in root of mean square volts can be transformed into maximum volts by multiplying by the proper factor. If we assume a sine form wave this factor is 1.41. Oscillograph curves of the E.M.F. show that a sine form is only approximated. The departure of this curve from a true sine form is such that variations in the readings obtained will hardly justify a further refinement in the matter of correction.

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[1] Warburg, Wied. Ann., lix., p. 1, 1896.

[2] Phil. Mag., December, 1905, p. 617.

[3] Wied. Ann., 1896, p. 676.

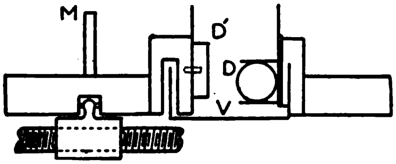

Fig. 1.

P.D.'s were obtained from a bank of incandescent lamps arranged in series. A General Electric transformer took current from a 110-volt 60-cycle circuit and stepped it up to 2,200 volts. This was passed through a bank of 44 incandescent lamps arranged in series. By introducing suitable lead wires, it was possible to utilize the fall in potential across one or more lamps. The transformer could be connected to give a total fall in potential of 550, 1,100 or 2,200 volts. Smaller steps than the direct drop across lamps could be obtained by shortcircuiting lamps outside the lead wires or by throwing lamps in parallel inside the lead wires. The small capacity and induction of the lamp filaments makes this a desirable means of obtaining P.D.'s.

Fig. 2 shows the manner of applying the P.D. to the electrodes *D*, *D'* across which the voltmeter *V* was connected. A suitable double-throw switch was arranged so that the galvanometer *G* could be placed in circuit to test for contact, or a P.D. applied.

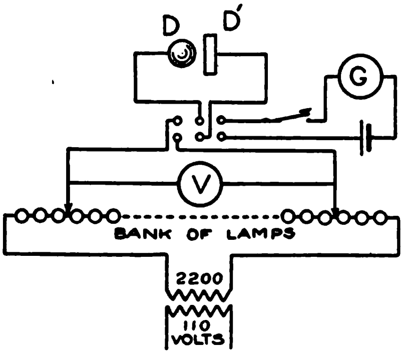

Fig. 2.

The method of procedure was to separate the surfaces a known distance and apply P.D.'s building up by small increments. The P.D. was applied for 5 seconds. If the medium did not break down a higher P.D. was applied and so on until a spark passed. This would be indicated by the deflection of the voltmeter needle.

The tables indicate both the values which the dielectrics would withstand and those at which they broke down. These are indicated on the graphical representation by a cross and circle, respectively.

## Results.

Plate I. (Fig. 3) represents graphically the results obtained on a transformer oil. This was purchased from a local concern as a low grade transformer oil.

This shows a bend in the curve corresponding to approximately 350 volts and at a distance lying between 13 and 15 micra. For distances below this elbow, the passage of a spark always produced coherence between the surfaces. No matter for how brief a time the P.D. was applied, a test with the galvanometer showed metallic contact between the surfaces. For distances above this bend such was not the case. The appearance of the surfaces in the two cases was noticeably different. For potentials corresponding to the flat portion of the curve, no discoloration of the surfaces or carbonizing

## TABLE I.

*Transformer oil.*

| Distance in Wave-lengths Sodium Light. | P.D. which Medium Would Withstand. | P.D. at which Medium Broke. | Distance in Wave-lengths Sodium Light. | P.D. which Medium Would Withstand. | P.D. at which Medium Broke. |
|---|---|---|---|---|---|
| 5 | 115 | 123 | 35 | 372 | 395 |
| 10 | 191 | 206 | 40 | 412 | 423 |
| 15 | 226 | 259 | 45 | 395 | 412 |
| 15 | 268 | 288 | 45 | 406 | 423 |
| 17.5 | 305 | 310 | 50 | 434 | 457 |
| 20 | 327 | 350 | 60 | 457 | 468 |
| 20 | 310 | 327 | 70 | 468 | 485 |
| 22.5 | 338 | 364 | 80 | 496 | 507 |
| 25 | 350 | 388 | 90 | 455 | 502 |
| 25 | 310 | 344 | 100 | 558 | 575 |
| 30 | 384 | 395 | 150 | 609 | 635 |
| 30 | 372 | 406 | 150 | 651 | 668 |
| 35 | 372 | 395 | 200 | 871 | 888 |

of the oil was observed, for distances greater than this critical distance both surfaces and oil were badly discolored and the surfaces pitted. This is characteristic of all the oils operated upon. Fresh oil was used after each discharge.

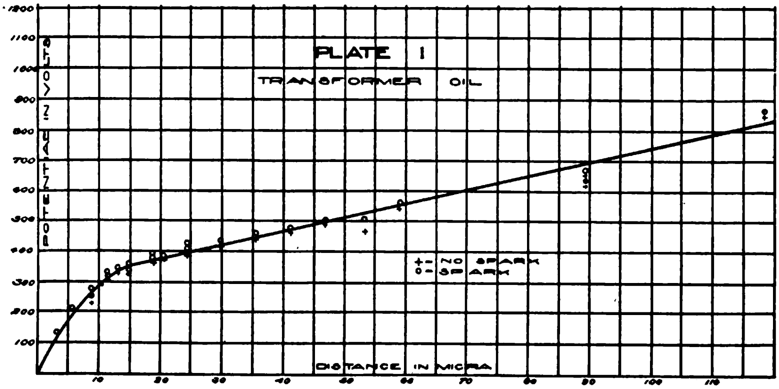

Fig. 3.

A series of readings was taken to determine if changes in the disruptive strength occurred after the passage of a spark. The results are shown in Table Ia.

In this case the surfaces were separated a distance of 40 wave-lengths (Na Light) or approximately 24 micra. The first reading was taken on a fresh oil, the second after a spark had passed during the time a switch could be closed and opened by the hand. This is designated as a quick spark. From the foregoing results, it would seem that the precaution of using a fresh oil after each discharge is unnecessary and that the oil is self-healing. The entire curve was repeated without renewal of the oil and practically the same results obtained. A second transformer oil sent out by one of the large electrical manufacturing companies gave the same result within the accuracy of the experiment.

### Table Ia.

| P.D. which Medium Would Withstand. | P.D. at which Medium Broke Down. | Condition of Medium. |
|---|---|---|
| 406 | 423 | Fresh oil. |
| 412 | 423 | Quick spark. |
| 406 | 420 | Quick spark. |
| 406 | 417 | Spark had passed 30 sec. |
| 406 | 429 | Spark had passed 60 sec. |

Table II. gives the results secured with kerosene oil. This was a high grade resistance kerosene. The results are given graphically in Fig. 4. A similar curve for air at atmospheric pressure is also

### Table II.

*Kerosene.*

| Distance in Wave-lengths Sodium Light. | P.D. which Medium Would Withstand. | P.D. at which Medium Broke Down. | Distance in Wave-lengths Sodium Light. | P.D. which Medium Would Withstand. | P.D. at which Medium Broke Down. |
|---|---|---|---|---|---|
| 5 | 79 | 110 | 35 | 417 | 451 |
| 5 | 56 | 112 | 40 | 389 | 411 |
| 7.5 | 129 | 136 | 45 | — | 451 |
| 10 | 182 | 203 | 50 | 423 | 451 |
| 10 | 169 | 226 | 60 | 451 | 474 |
| 12.5 | 268 | 299 | 70 | 451 | 474 |
| 15 | 268 | 299 | 80 | 552 | 564 |
| 17.5 | 322 | 328 | 90 | 564 | 592 |
| 20 | 327 | 347 | 100 | 592 | 620 |
| 25 | 350 | 389 | 150 | 810 | 850 |
| 30 | 389 | 411 | 200 | 980 | 1,020 |

given. It is interesting to note that, for the distances taken, air is the better insulator. Mr. Steinmetz' prediction on this point has been noted previously. It is well known that the air curve bends toward the *X*-axis and it is presumed that the curve representing the disruptive strength of a liquid is a straight line. At the point of intersection the spark-potentials would be equal. MacFarlande and Pierce[1] gave this as 1 mm. for air and kerosene.

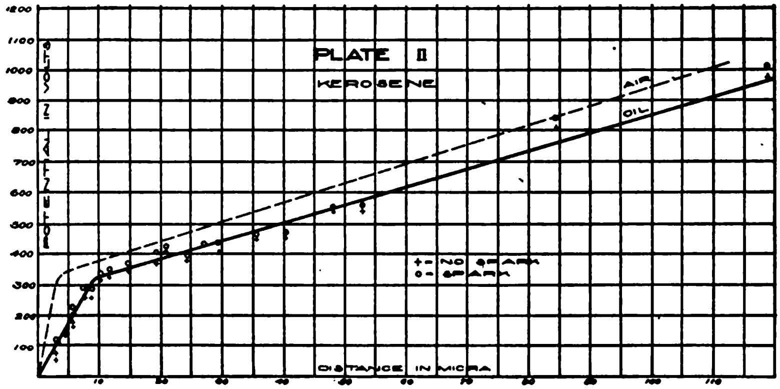

Fig. 4.

If this curve for kerosene is exterpolated the potential gradient at 1 cm. would give 55 kilo-volts per cm. This requires an exterpolation of the curve to something like 80 times its length and is unwarranted, however, it agrees well with the value obtained by MacFarlande, which was 50 kilo-volts per cm.

Plate III. (Fig. 5) represents the results obtained with paraffin oil. This shows a potential gradient somewhat less than that of kerosene and does not agree with MacFarlande's value of 87 kilo-volts per cm.

Paraffin oil, however, is a trade name applied to a number of the petroleum products. Oils sold under this name vary from heavy viscous oils to extremely limpid ones. The oil operated upon, in this case, was a clear limpid oil prepared by a drug firm and sold to the medical trade under the name of petrolatum oil. It may be observed that the curves representing the petroleum products show similar values and so far as their disruptive strength is concerned one is practically as good as another.

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[1] Physical Review, Vol. I., p. 165.

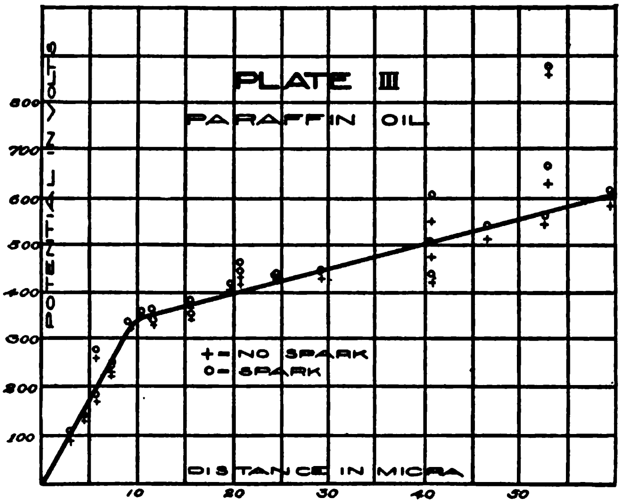

Fig. 5.

## Table III.

*Paraffin Oil.*

| Distance in Wave-lengths Sodium Light. | P.D. which Medium Would Withstand. | P.D. at which Medium Broke Down. | Distance in Wave-lengths Sodium Light. | P.D. which Medium Would Withstand. | P.D. at which Medium Broke Down. |
|---|---|---|---|---|---|
| 5 | 92 | 110 | 35 | 434 | 451 |
| 7.5 | 127 | 135 | 40 | 412 | 446 |
| 10 | 265 | 282 | 40 | 485 | 508 |
| 10 | 164 | 188 | 45 | 451 | 462 |
| 12.5 | 226 | 254 | 45 | 462 | 474 |
| 12.5 | 234 | 245 | 50 | 412 | 440 |
| 15 | 327 | 350 | 60 | 479 | 508 |
| 15 | 311 | 344 | 70 | 479 | 508 |
| 17.5 | 271 | 282 | 70 | 423 | 440 |
| 17.5 | 377 | 389 | 70 | 547 | 609 |
| 20 | 333 | 344 | 80 | 508 | 547 |
| 20 | 344 | 361 | 90 | 540 | 558 |
| 25 | 310 | 338 | 90 | 620 | 661 |
| 25 | 355 | 378 | 90 | 863 | 884 |
| 30 | 400 | 411 | 100 | 558 | 630 |
| 30 | — | 406 | | | |

Plate IV. (Fig. 6) shows the results secured with olive oil, the only vegetable oil used in the test. It shows a higher potential gradient than any of the others. The bend in this curve is not so

## TABLE IV.

*Olive Oil.*

| Distance in Wave-lengths Sodium Light. | P.D. which Medium Would Withstand. | P.D. at which Medium Broke Down. | Distance in Wave-lengths Sodium Light. | P.D. which Medium Would Withstand. | P.D. at which Medium Broke Down. |
|---|---|---|---|---|---|
| 5 | 59 | 94 | 30 | 384 | 390 |
| 5 | 55 | 94 | 35 | 406 | 429 |
| 7.5 | 113 | 118 | 35 | 406 | 446 |
| 10 | 149 | 164 | 40 | 440 | 457 |
| 10 | 164 | 169 | 40 | 448 | 468 |
| 12.5 | 175 | 186 | 45 | 491 | 513 |
| 15 | 175 | 223 | 45 | 505 | 513 |
| 15 | 155 | 178 | 50 | 550 | 592 |
| 17.5 | 223 | 240 | 60 | 584 | 626 |
| 20 | 271 | 293 | 70 | 546 | 626 |
| 22.5 | 288 | 310 | 70 | 632 | 643 |
| 25 | 342 | 388 | 80 | 685 | 711 |
| 25 | 372 | 384 | 90 | 744 | 792 |
| 27.5 | 388 | 416 | 100 | 792 | 843 |

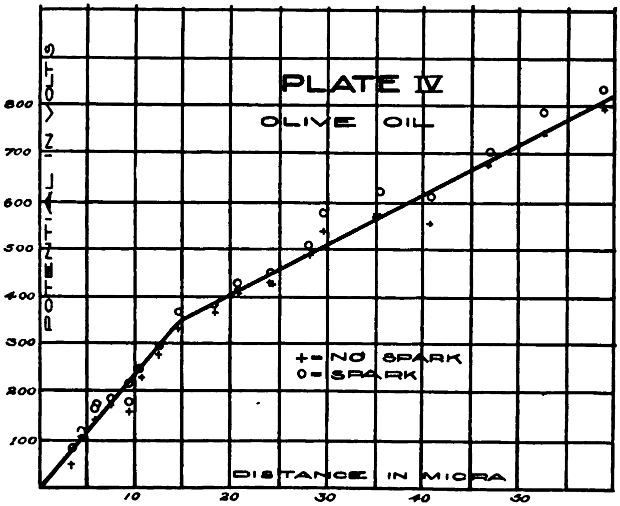

Fig. 6.

apparent. There is some evidence of a turning point at a P.D. of 350 volts, at which coherence between the plates ceased.

An attempt was made to secure readings with water as a dielectric. Platinum electrodes were used in a high grade of ammonia-free distilled water. This was a complete failure. The problem of securing a suitable water in the quantities desired seems very difficult, in the light of the Kohlrausch experiments on water. The conductivity of this water was not measured on account of the failure to obtain results.

## CONCLUSIONS.

These experiments on the limited number of oils used would indicate :

1. That the potential gradient for very small distances is higher than for large ones.

2. That for small distances air is a better insulator than liquid dielectrics.

3. That the potential at which the bend in the potential-distance curve occurs is the same for air and liquid dielectrics.

If we accept Professor J. J. Thomson's explanation of the mechanism of spark discharge in gases for potentials less than the "minimum potential," *viz.*, that free metal corpuscles are the carriers of the discharge, and attach a similar meaning to the elbow occurring at the same voltage in liquids, it would follow that the corpuscles were able to travel further in liquids than in gases.

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# HYDRATION IN SOLUTION.

BY C. S. HUDSON.

IN the present article the formation of hydrates and their anhydrides in solution is considered and an explanation is attempted of some of the general phenomena of hydration, such, for example, as the occurrence of transition temperatures, the equality of solubilities at these temperatures, and the fact that the stable substance always has the smaller solubility. The explanation that I give of these general facts is based on the observations of the hydration of milk-sugar that I have published.[1]

## 1. THE RELATED SOLUBILITIES OF A TYPICAL HYDRATE, MILK-SUGAR, AND ITS ANHYDRIDE.

Suppose an anhydrous substance $A$, for example anhydrous milk-sugar, to form with water a single hydrate $H$, hydrated milk-sugar. The reaction which takes place in dilute solution between these two substances can be represented by the symbol of a balanced reaction.

$$A \rightleftharpoons H, \tag{1}$$

if the constant mass of the reacting water is omitted for brevity. If the initial solubility of $A$ at a chosen temperature is $s_a$, and the concentration of $H$ that is in equilibrium in solution with $s_a$ of $A$ is $C_h$, the final solubility of $A$ is

$$S_a = s_a + C_h. \tag{2}$$

In like manner the final solubility of the hydrate is

$$S_h = s_h + C_a. \tag{3}$$

Since it has been shown by Nernst[2] that the proportion of hydrate that is in equilibrium with anhydride is nearly independent of concentration we may write as a close approximation

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[1] Princeton Bulletin, April, 1902. Zeitschrift für physikalische Chemie, 44, 487–494 (1903); 50, 273–290 (1904). Journal of the Americal Chemical Society, 26, 1065–1082 (1904).

[2] Zeitschrift für physikalische Chemie, 11, 345 (1893).

$$C_h/s_a = s_h/C_a = K. \tag{4}$$

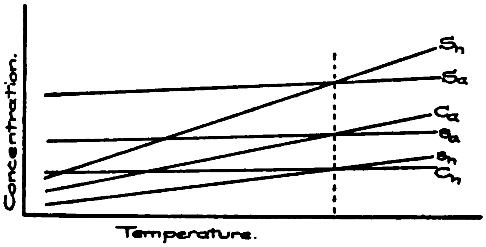

Fig. 1.

In the accompanying figure the quantities that occur in the three equations are represented over a range of temperature. Three of these lines can be drawn at will for a typical substance, but the others are then determined by the positions of these three. I have drawn $s_a$, $s_h$ and $S_h$ from the solubility data of milk-sugar.

It follows from the equations (2), (3), and (4) that

$$S_a \gtreqless S_h \text{ and } C_h \gtreqless s_h \text{ when } s_a \gtreqless C_a. \tag{5}$$

This relation, and also the figure, shows how it is that one of the substances *A* and *H* is stable at a chosen temperature in the presence of water while the other is unstable, and also shows which of the substances is the stable one. Thus, for example, if it is known that $s_a > C_a$ it is to be concluded that the hydrate is the stabler form, for since $C_h > s_h$, the finally saturated solution of anhydride contains hydrate in greater concentration than that corresponding to the initial solubility of the hydrate and is thus supersaturated with respect to the hydrate; on the other hand, since $C_a < s_a$, a finally saturated solution of the hydrate contains anhydride in less concentration than its initial solubility, and such a solution is undersaturated with respect to the anhydride and is stable. Or, briefly, we may say that the stable substance is the one whose initial solubility is greater than its concentration in the finally saturated solution of the other substance. This definition of the stabler substance leads from (5) to the conclusion that the unstable substance in the case of hydrates and anhydrides has the greater final solubility, a fact that is of the most common experience and which Van't Hoff[1] and Ostwald have proved holds for all substances. It is instructive to notice that though there is the necessity in the definition of the unstable substance that it have the greater final solubility, there is, on the contrary, no such relation between stability and initial solubility. This conclusion is evident when the equations (2), (3) and (4) are reduced to the form

$$s_a/s_h = S_a/S_h(1/K). \qquad (6)$$

Since $K$, the equilibrium constant of the hydration reaction, is not known to depend on the relative stability of the two substances, it is not possible to decide from a knowledge of their relative stability anything regarding their initial solubilities.

## 2. The Transition Temperatures of Hydrates.

The relations shown by the equations (2), (3) and (4), and represented in the figure, also lead to a simple view of what takes place in a solution of a hydrated substance at its transition temperature. To show this we may first sum up the properties of such a solution that are peculiar to this temperature; they are, equality of the final solubilities of the hydrate and the anhydride, identity of the two resulting solutions, and equality of the vapor pressure of these solutions with that of a mixture of solid hydrate and anhydride. I know of no molecular-kinetic explanation of the last one of these general properties, but the first two receive a clear explanation from the equations and the figure, as follows: At whatever temperature $C_a = s_a$, $C_h = s_h$ and $S_a = S_h$, from (5). At this temperature, therefore, which may be defined the transition temperature,[2] the two substances have the same final solubility and also give solutions which contain the same substances in the same concentrations, and are therefore identical, which was to be shown.

If this is the correct explanation of the peculiar properties of solutions at the transition temperatures we should not expect at these temperatures any sudden or discontinuous change in any property of the solution, because the same substances exist in solution below, at and above the transition temperature, and the relative concentrations of these substances change gradually and continuously with the temperature. There is indeed no evidence at all that supports the alternative hypothesis, which is now generally abandoned, that below the transition temperature only the one form exists in solution, and above this temperature only the other form. It is certainly a more rational view to assume that both above and below this temperature both or indeed all forms of the substance exist together in solution, their concentrations and initial solubilities being related in the manner that has been indicated.

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[1] Vorlesungen, 1903, II., p. 127.

[2] It has already been shown by Van't Hoff, Vorlesungen, 1898, I., 219, that at transition temperatures the concentrations of the substances in saturated solution are equal to their initial solubilities.

## 3. THERMODYNAMICS OF HYDRATION REACTIONS.

The solubility relations that are shown by the figure receive additional interpretation from the application to them of thermodynamic principles.

To begin with, let the free energy of the isothermal formation of solid hydrate from solid anhydride and water be calculated. This hydration can proceed reversibly in three ways, namely, by isothermal distillation of water, and by dissolution of anhydride and water in, and crystallization of hydrate from, saturated solutions of anhydride and hydrate respectively.

### *a. Hydration by Distillation.*

If the vapor pressure of pure water at absolute temperature $T$ is $p_w$ and the pressure of the aqueous vapor that is in equilibrium with a mixture of solid hydrate and anhydride is $P_h$, then by isothermal evaporation of the water, expansion from $p_w$ to $P_h$, and condensation on the solid anhydride, the hydrate can be produced isothermally and reversibly with the gain per mol of hydrate produced of the work,

$$W = nRT \log p_w/P_h, \tag{7}$$

where $n$ is the number of molecules of water that occur in the hydrate.

### *b. Hydration by dissolution in saturated anhydride solution.*

Imagine a reservoir composed of a finally saturated solution of the anhydride, containing anhydride and hydrate in the concentrations $s_a$ and $C_h$ respectively. Draw out from this reservoir through a wall that is permeable for the solvent and the hydrate but impermeable for the anhydride one mol of hydrate at the constant concentration $C_h$, and at the same time allow one mol of anhydride to dissolve into the reservoir and $n$ mols of water to evaporate at $p_w$, to expand to $p_a$, the vapor pressure of the saturated solution of the anhydride, and then to condense into the reservoir. The mol of withdrawn hydrate is then to be concentrated from $C_h$ to $s_h$, the initial solubility of the hydrate, and crystallized from the solution. The final change that is produced by this process is the conversion of solid anhydride and water to solid hydrate because the reservoir remains unaltered, and the free energy of the hydration per mol of hydrate formed is

$$W = nRT \log (p_w/p_a) + RT \log (C_h/s_h). \tag{8}$$

*c. Hydration by dissolution in a saturated hydrate solution.*

By a process similar to the foregoing one dissolve one mol of anhydride at concentration $s_a$ in water, concentrate it to $C_a$, and press it into a saturated solution of the hydrate; at the same time distil $n$ mols of water into the saturated solution and crystallize from it one mol of hydrate. The free energy by this method of hydration is

$$W = nRT \log (p_w/p_h) + RT \log (s_a/C_a). \tag{9}$$

Since the three expressions (7), (8), and (9) for the free energy are equal it follows that

$$(p_w/P_h)^n = (p_w/p_a)^n(C_h/s_h) = (p_w/p_h)^n(s_a/C_a). \tag{10}$$

If we select as the distinguishing property of the transition temperature the fact that at it the finally saturated solutions of anhydride and hydrate respectively are identical, it follows that $p_a = p_h$ and therefore $C_h = s_h$ and $s_a = C_a$, which is the conclusion that has already been obtained in section (2). Also, since at this temperature $C_h/s_h = s_a/C_a = 1$, it follows that $P_h = p_a = p_h$, which expresses another general property of hydrates at their transition temperatures; as stated before, no molecular-kinetic explanation of this relation is known.

At temperatures other than that of transition the general fact that $P_h$ is less than $p_a$ or $p_h$ below the transition temperature and greater above it can be used to determine which is the stable substance. For it follows from (10) that above the transition temperature, since $P_h$ is greater than $p_a$ or $p_h$, $C_a$ is greater than $s_a$ and $s_h$ is greater than $C_h$, and therefore the anhydride is stable in the presence of its saturated solution. Similarly it can be shown that the hydrate is the stable substance below the transition temperature.

These conclusions from the thermodynamic relations agree completely with those already obtained from the solubility curves of the figure, which are based on the data for the solubility of milk-sugar. But the thermodynamic relations can give us further information which is not evident from the solubility curves. This is discussed in the two following sections.

### 4. A METHOD OF CALCULATING THE SOLUBILITY OF SOME SUBSTANCES THAT FORM HYDRATES.

It is evident from (10) that

$$(p_a/P_h)^n = C_h/s_h, \tag{11}$$

and

$$(p_h/P_h)^n = s_a/C_a. \tag{12}$$

Since $p_a$, $p_h$, and $P_h$ are usually measured with ease, these equations give a means of calculating the initial solubility of those substances for which $C_h$ or $C_a$ can be determined. For example, let the initial solubility of anhydrous milk-sugar at zero centigrade be calculated. Here $n = 1$, $C_a = 20$ millimols per 100 grams of water,[1] $P_h = 0.46$ cm. mercury nearly, since the saturated solution at zero is of 0.3 molal concentration and its vapor pressure is nearly the same as that of water, and I find $P_h$ to have the values 43.3 at 90°, 7.2 at 60°, giving by extrapolation with the formula of Clausius, $P_h$ at 0°, 0.062 cm. From these data $s_a$ is calculated from (12) to be 148 millimols per 100 grams of water. By experiment I have found $s_a$ to be 125. The agreement is as good as could be expected, considering the large possible error in the determination of $P_h$, which cannot be observed at 0° on account of the sluggishness of its establishment.

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[1] Journal American Chemical Society, **26**, 1074 (1904).

It is noteworthy that in the experimental determination of the quantities from which $s_a$ is calculated it is not necessary to isolate the anhydride. Only in the determination of $P_h$ from a partially dehydrated sample of the hydrate is it needful to have the anhydride in the solid state and it is here mixed with hydrate in such an intimate manner that it cannot be described as isolated.

## 5. THE INFLUENCE OF FOREIGN SUBSTANCES ON THE SOLUBILITY OF HYDRATES AND THEIR ANHYDRIDES.

If the free energy of the hydration reaction that is described in section (3) be calculated by a method which is a combination of those under (*b*) and (*c*), employing a reservoir of an unsaturated solution containing hydrate in concentration $c_h$ and anhydride in concentration $c_a$ and having a vapor pressure $p_s$, it is found that per mol of hydrate formed the energy is

$$W = nRT \log p_w/p_s + RT \log s_a/c_a + RT \log c_h/s_h. \qquad (13)$$

If this value is put equal to (7),

$$\frac{c_h}{c_a(p_s)^n} = \frac{s_h}{s_a(P_h)^n}, \qquad (14)$$

which is independent of the concentration.

As Nernst[1] has pointed out, since the vapor pressure of a dilute solution changes only very slightly with the concentration, equation (14) shows that the ratio of hydrate to anhydride is nearly constant in dilute solution, particularly if $n$ is small. It is, however, to be expected that when $n$ is large there will be an appreciable decrease of the ratio of hydrate to anhydride if the vapor pressure lessens. For example, if a chosen dilute aqueous solution at 20° contains a dekahydrate and its anhydride in equilibrium in the ratio $c_h/c_a = 1.50$, the addition of a foreign substance in tenth molal concentration would be expected to change the vapor pressure of the solution, according to Raoult's law, from 1.750 cm. mercury to 1.747 cm., which by (14) would change $c_h/c_a$ from 1.50 to 1.47, an alteration of 2 per cent. Although the magnitude of such changes of hydration equilibrium is small, it is nevertheless sufficient, as I have shown at another place,[1] to account quantitatively for the lowered freezing temperatures of solutions, which are not inconsiderable depressions. I shall seek now to show that such changes of hydration equilibrium may also be the cause of well recognized regularities in the change of solubility of hydrates and anhydrides that occur when other, apparently indifferent, substances are present in the solution.

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[1] Loc. cit. Equation (14) differs from the similar one obtained by Nernst in the respect that the factors which compose Nernst's constant are here separated and identified with other physical quantities.

First, to determine the character of these regularities. I regard the best evidence on the change of solubility of hydrates to be that given by the experiments and the theory of Goldschmidt,[2] which he has summed up in the phrase "the molecular increase of solubility of hydrates."

These experiments give the solubility at room temperature of the bi- and tetra-hydrates of sodium paranitrophenolate in pure water and in molal solutions of urea, glycerine, acetone, propionitrile, acetonitrile, urethane and alcohol. It was found that all the solutions except the alcoholic dissolve more hydrate than does pure water, that the increase of solubility is nearly constant for the same hydrate in the different solutions, and that the ratio of increase of solubility of tetrahydrate to that of bihydrate is a constant 1.02.[3] The experiments of Löwenherz[4] also give evidence on the change of solubility of hydrates. He found that urea causes hardly a measurable change in the solubility of sodium sulphate dekahydrate, but a large decrease (13 per cent.) in the solubility of anhydrous sodium sulphate. To sum up then, it is found that the solubility of hydrates is frequently increased by foreign substances, never markedly decreased, and that the higher hydrate shows a greater increase of solubility than the lower.

The extensive evidence on the change of solubility of anhydrides has also been expressed in the form of a general regularity, namely, that the solubility of anhydrides is decreased by the presence of foreign substances,[1] which in most of the experiments, have been salts.

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[1] PHYSICAL REVIEW, 21, 16 (1905).

[2] Zeitschrift für physikalische Chemie, 17, 145 (1895).

[3] Goldschmidt has given a theory of this change of solubility, and from it has calculated this ratio to be 1.02, in full agreement with observation. For the details of this instructive theory, which in many respects is similar to the one here given although their initial assumptions are different, I refer to Goldschmidt's article.

[4] Zeitschrift für physikalische Chemie, 18, 70 (1895).

It can be shown that these changes of solubility are to be expected from theoretical considerations, as follows: If a typical anhydrous substance $A$ forms a series of hydrates in solution, its final solubility can be expressed as

$$S_a = s_a + C_{h_1} + C_{h_2} + C_{h_3} + C_{h_4} + \cdots$$

where the numerical subscripts denote the number of molecules of water in the hydrate. A relation of the form of (14) connects $s_a$ and each $C_h$, and it is evident from (14) that the dissolution of a foreign substance in the solution and the accompanying decrease of vapor pressure of the solution will change the final solubility of $A$ to

$$S_a' = s_a + C_{h_1}' + C_{h_2}' + C_{h_3}' + C_{h_4}' + \cdots$$

where each $C_h'$ is less than the corresponding $C_h$, and $S_a'$ therefore less than $S_a$. Thus there is to be expected a decrease in the solubility of anhydrous substances which form hydrates in solution caused by the presence of foreign substances in solution, a conclusion that agrees with the previously mentioned observed regularity of anhydrides.

The final solubility of a hydrate, $H_3$ for instance, in water can be expressed as

$$S_{h_3} = C_a'' + C_{h_1}'' + C_{h_2}'' + s_{h_3} + C_{h_4}'' + \cdots$$

and its solubility in a solution of a foreign substance

$$S_{h_3}' = C_a''' + C_{h_1}''' + C_{h_2}''' + s_{h_3} + C_{h_4}''' + \cdots$$

It is evident from (14) that the concentration of the anhydride and those of the hydrates of lower water content than $H_3$ are increased by the presence of the foreign substance, but that the concentrations of the hydrates higher than $H_3$ are decreased. Two effects therefore oppose each other and it is not clear whether the final solubility of the hydrate will be lessened or raised by the foreign substance. On the other hand if the solubility equations of a higher hydrate are expressed as has been done for $H_3$, it is evident that the number of substances whose concentration is increased is greater and the number whose concentration is decreased is less for the higher hydrate, and it is to be concluded therefore that at temperatures where the two hydrates give saturated solutions of nearly the same concentration, the higher hydrate will show a greater tendency to increase in solubility in a solution of a foreign substance. This conclusion is strictly applicable only to hydrates at their transition temperatures, because it is only at these temperatures where the two solutions are identical that the relative change of solubility of the two hydrates can be determined by the relative number alone of dissolved substances whose concentrations are increased or decreased by the foreign substance. The conclusion agrees with the previously mentioned experiments of Goldschmidt which show that foreign substances increase the solubility of a tetra-hydrate to a greater extent than that of a bi-hydrate.

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[1] Rothmund, Zeitschrift für physikalische Chemie, 33, 401 (1900). Rothmund has used the word "nonelectrolyte," but it is apparent that the substances whose solubility is decreased may be equally well classed as "anhydrides."

The theoretical conclusions regarding the influence of foreign substances on the solubility of hydrates and their anhydrides thus agree in a clear and natural manner with well-established and hitherto unexplained facts.

The solubility of many gases, oxygen, hydrogen, nitrogen, for example, is less in solutions than it is in pure water. As these gases are all anhydrous substances, it is possible that their decrease of solubility is due to their being markedly hydrated in solution. True, the solutions that have been examined are mostly electrically conducting salt solutions, in which complications are likely to occur, such as electrostriction,[1] which are here not considered at all. Nevertheless, most of the few experiments on solutions of non-electrolytes indicate in the same manner the formation of hydrates of these gases in solution.

## 6. DISCONTINUOUS CHANGES OF MELTING AND POLYMORPHISM.

The explanation of some of the peculiarities of the transition temperatures of hydrates that I have attempted assumes that the substance that is unstable in the solid state is nevertheless stable in solution, and that the formation of hydrate or anhydride which takes place discontinuously in the solid state at one temperature and pressure occurs in solution over a wide range of temperature and pressure. The discontinuity of such transition reactions as opposed to the continuous formation of most substances over a range of temperature, as, for example, the production of hydriodic acid from its elements, is so often emphasized that it seems to me important to understand that the discontinuity of the chemical change does not follow as a consequence of the discontinuity of the formation of the phases. The only reactions that take place at one temperature only are the transition reactions and the meltings. I have here endeavored to show that the transition of hydrates, and what is true of these transitions is quite applicable to all transitions, are not discontinuous in solution, and at another place[1] I have shown that the melting phenomena can also be clearly and quantitatively accounted for on the hypothesis that the solid exists dissolved in the liquid, like any ordinary solution, over a wide range of temperature, or, in other words, that the chemical reaction which gives rise under appropriate conditions of temperature and pressure to the phenomena of melting is quite similar to the ordinary balanced chemical reactions and are like these continuous, though some of its effects appear discontinuous. There is no example, as far as I know, of a chemical reaction which occurs at one temperature only.

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[1] Drude and Nernst, Zeitschrift für physikalische Chemie, 15, 79 (1894). Nernst, Theoretische Chemie, 1900, 445.

## 8. SUMMARY.

The contents of this article may be summarized as follows:

The initial and final solubility curves for anhydrous and hydrated milk-sugar give an instructive view of the relations that cause the transition temperatures of hydrates. This theory, in which the two substances are regarded as present in equilibrium in solution over a wide range of temperature, shows how it is that the stable form has the smaller solubility and that there is no discontinuity in the properties of the solution at the transition temperature.

A thermodynamic theory of a typical hydration reaction is worked out, which expresses the relations of concentration and solubility that give rise to transition temperatures, leads to a method of calculating solubilities which is found to give an accurate value for milk-sugar, and forms the basis of an extension of Goldschmidt's theory of the influence of foreign substances on the solubility of hydrates.

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[1] PHYSICAL REVIEW, l. c.

Evidence is given that the discontinuous physical changes of state such as melting and transition, are the results of chemical changes (*i. e.*, the formation of new molecules) which are themselves continuous over a wide range of temperature.

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# EVERY-DAY PROBLEMS OF THE MOVING COIL GALVANOMETER.

BY WALTER P. WHITE.

ALL moving coil galvanometers, when critically damped by the coil alone, are, for small deflections, equally effective in utilizing the energy of the source of current[1]; their efficiency as galvanometers depends on the deflection obtained with a given amount of energy, and therefore on the smallness of the controlling force. The work done by twisting the suspending wire during deflection bears a constant ratio to that expended during the same time[2] in heating the circuit with the coil at rest; that is,

$$\tfrac{1}{2}\vartheta^2 Q = .157\ I^2RT. \tag{17}$$

This energy equation,[3] by a change to practical units, becomes identical with the sensibility equation,

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[1] W. P. White, Sensitive Moving Coil Galvanometers, PHYS. REV., 19, 304, 1905.

[2] With a critically damped galvanometer 99 per cent. of the deflection is executed in the periodic time $T$. Hence this time may often be taken as the time the observer must wait to get his reading, and the time in which the current energy is expended. .999 of the deflection is completed in the time 1.5 T.

[3] The notation and the numbering of the equations are here consistent with the former article, *e. g.*:

Let $K$ be the moment of inertia.
$Q$, the moment of torsion of the controlling force.
$I$, the current in microamperes.
$\theta$, the angular deflection in two-thousandths of a radian.
$R$, the resistance of the whole circuit in ohms.
$R'$, the the resistance of the coil.
$H$, the mean effective field strength.
$l$, the length of the vertical wire in the coil.
$r$, half the width of the coil.
$G$, $= Hlr$, the dynamic constant.
$T$, the undamped period.
$D'$, $= G^2/R$, the damping coefficient of the coil.
$D$, $= 2\sqrt{KQ}$, the total damping coefficient necessary for critical damping.
$S$, $= \theta/I$, the current sensibility in megohms.
$V$, $= S/R$, the corresponding voltage sensibility.
Equation (17), alone, is in absolute units.

$$S^2 = 12.6\frac{RT}{Q}. \tag{11}$$[1]

In the slightly different form :

$$V^2R\frac{1}{T} = \frac{12.6}{Q} \tag{18a}$$

the energy equation shows immediately, on the right hand side, the actual efficiency of the galvanometer; and suggests more directly the general problem of galvanometer work, which is to make the best possible combination of *all three* factors in the left hand member. The deflection for a given amount of energy and the normal-sensibility are each proportional to the square root of the second member. $R$ is here the critical resistance.

*The Second Condition.* — This is expressed by the familiar equation

$$4\pi^2K = T^2Q. \tag{1}$$

Combining the last two equations, we get

$$V^2R\frac{1}{T^3} = \frac{.32}{K} \tag{19a}$$

which is more convenient than (18*a*) when $T$ is varied without changing $K$; that is, by varying the stiffness of the suspending wire.

*Light Coils.* — In this latter case, inspection of the equation shows that for an increase of period the sensibility increases still more rapidly, nearly as much, in fact, as in the same adjustment with galvanometers of the Kelvin type.[2] The advantage, then, of lengthening the period by reducing the stiffness of the suspension is relatively great. In the case (equation 18*a*) where the coil is enlarged, the sensibility only increases as the square root of the period. Reducing the suspension increases the efficiency of the galvanometer, as well as the period. Increasing the moment of inertia of the coil leaves the efficiency unaltered and merely increases the sensibility at the expense of a disproportionately protracted period. There is, therefore, nearly always a decided advantage to the user of a galvanometer in making the coil small. The only exception is where high sensibility is indispensable, and (after the suspension has been reduced to its smallest value) must be secured by greatly increasing both the size of coil and the period. In all other cases a heavy coil causes an unnecessary waste of time. If the suspension has at the same time its minimum value, the disadvantage of the increased period is partly offset by greater sensibility, though this is seldom worth what it costs; if both coil and suspension are heavy, there is practically no compensating advantage.

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[1] Jaeger was apparently the first to give simple equations of this form. Zeitsch. fur Instrumentenkunde, 23, 261, 1903. Many important questions relating to the moving coil galvanometer are discussed in this article.

[2] The difference is due to the necessity of preserving critical damping with one instrument and not with the other. See also the previous article, p. 311.

$K$ has been made as small as .03 c.g.s. units without difficulty (see other article, p. 316), and a value of .05 units would, therefore, seem often attainable. Larger values for $K$ are needed where the critical resistance is high (see p. 385 below). The smallest value of $K$ of which I have been able to learn in a commercial instrument is .25 c.g.s. units, and some firms advertise instruments whose smallest value of $K$ is over 1.5 units. Suspensions can readily be purchased giving a value of $Q$ as small as .18 c.g.s. units.

*The Third Condition, and the Magnet Strength.*—A further limiting condition is found in the requirement of critical coil damping. A convenient statement of this condition for the moving coil galvanometer is obtained by combining equations (13) and (16), which gives

$$H = A\sqrt{\frac{R}{R'T}} \tag{20a}$$

where $A$, nominally a constant, varies slightly with the inert material in the coil, which was neglected in setting up the original equations. Postponing for a moment the consideration of its variations, we reach the following results:

(1) The sensibility is not directly dependent upon the field strength. In general, an unduly weak field will not prevent a galvanometer from being made sensitive.

(2) The period, however, except for the somewhat limited variations possible in the ratio $R/R'$, depends almost entirely upon the field strength. The shortness of period possible with a light coil requires also a strong magnet. Weak magnets tend to make galvanometer work unnecessarily tedious.

(3) A high external resistance increases the difficulty of securing a short period, and may demand an increase in the field strength.

(4) If the internal resistance is increased, the field strength may, other things being equal, be diminished, and conversely. These two quantities are therefore to a certain extent substitutes for each other. An increase in the coil resistance, however, often reduces the sensibility undesirably. It is least detrimental where most needed, that is, when the external resistance is high. Another obstacle to an increase of $R'$, however, is set by the size of the coil. The physical interpretation of the value of $R'$ in this connection is, of course, that $R'$ serves as a measure of the number of turns of wire in the coil. To increase it with a given coil demands the use of finer wire, and when the limit of fineness is reached, any further increase necessitates making the coil heavier. The most sensitive galvanometers, therefore, that is, those with the smallest coils, will require the strongest fields, and this requirement will be greater the shorter the period and the higher the external resistance.

By the method used in getting equation (16) it can be shown that the largest value of $R'$ is, to a rather rough approximation, 680 $K/r_2$ if the finest available wire is 1½ mils in diameter.

For $A$ equal to 750, a fair average value, Table I. shows the field strength necessary to give different periods when the resistance of the coil is $\frac{1}{7}$, and 1, 2 and 3 times that of the external circuit, that is, for $R/R' = 8, 2, \frac{8}{2}$ and $\frac{4}{3}$.

### Table I.

*Approximate field strength required to give different periods for various ratios of coil and total resistance.*

| $T$ | $\frac{R}{R'} = 8$ | $\frac{R}{R'} = 2$ | $\frac{R}{R'} = \frac{3}{2}$ | $\frac{R}{R'} = \frac{4}{3}$ |
|---|---|---|---|---|
| 1 second. | 2106 lines. | 1053 | 920 | 870 |
| 2 " | 1500 " | 750 | 650 | 613 |
| 3 " | 1220 " | 610 | 530 | 500 |
| 4 " | 1050 " | 525 | 460 | 433 |
| 8 " | 750 " | 375 | 325 | 308 |

In a number of galvanometers of American manufacture, $H$ varied from 200 to 600 lines.

*Zero Shift.*—The fear of the detrimental magnetic effect is sometimes given as a reason for employing the weak magnets often favored by instrument-makers. Equation 20 leads to a convenient statement of the conditions governing this effect. The magnetic attraction has been shown (page 314, of the former article) to be, for a given per cent. of magnetic impurity, proportional to the square of the field strength, and to the mass of the coil, regardless of its shape or dimensions. The detrimental effect on the readings is proportional to this quantity divided by the controlling force; that is, if $M$ is the detrimental effect, and changes in the form of the coil are excluded,[1]

$$M \propto \frac{H^2K}{Q}, \text{ or } M \propto H^2T^2. \tag{21}$$

By combination with equation (20) we get, for critical coil damping,

$$M \propto TA^2\frac{R}{R'}. \tag{22}$$

Increase in field strength, therefore, when used to shorten the period, so far from increasing, diminishes the detrimental effect.

The magnetic effect is detrimental in two ways. First, it tends to keep the coil in a fixed position, and hence increases the controlling force. This of course does very little harm except where maximum galvanometer efficiency, and, therefore, the minimum value of the controlling force, is required. The second effect, of far less magnitude, is in general much more important, namely, the shifting of the zero after deflection, which results from a slight change in the direction of magnetization of the coil.

The importance, in this particular connection, of magnet strength can easily be exaggerated. The detrimental effect is generally chargeable to the coil. With reasonably good coils, it is troublesome only in the strongest fields and should not be perceptible with magnets of ordinary strength. For instance, in a Leeds and Northrup H-form galvanometer, with cast-iron magnet and open field of 420 lines,[1] the zero shift could not be detected, that is, it was certainly less than .01 per cent. The same was true of a Siemens & Halske galvanometer, with a radial field of about 1,300 lines and 8-second period.[2] The control was here increased more than 30 per cent. On the other hand, in a galvanometer of a type much advertised in the nineties, where the coil and suspending wires were enclosed in tubes, a magnet built up of small steel horseshoes, presumably to secure special field strength, barely gave 200 lines. The coil weighed 16 grams and required an auxiliary damper to bring it to rest in 24 seconds. After an excessive deflection the spot of light usually took an appreciable fraction of an hour to get back to the scale at all, so great was the zero shift. The fact that this instrument is less than seven years old shows what gratifying progress has recently been made in galvanometer construction. It is still true, however, that except where extreme sensibility is needed, the periods of many instruments are too long and the magnets too weak. The case of the H-form cast-iron magnet just mentioned, whose field gave very large clearance for the coil and was not especially uniform, shows that the detrimental magnetic effect need not be serious for fields of a thousand lines, and therefore the field of a first-class galvanometer should not be less than this, except where the period is such as to render a weaker magnet actually desirable.

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[1] $M$ is of course less for the same $K$ as the coil becomes wider. See page 315 of the former article.

A moving coil galvanometer consists essentially of a magnet, a coil, and a suspending wire. If the period is long, all difficulty in constructing either coil or magnet disappears. The value of the instrument then depends mainly on the suspension, and therefore, for the most part, on the wire manufacturer, and not the instrument-maker. The galvanometers of ten years ago are therefore fairly sensitive, and, were it not for their remarkably weak fields, would in this respect nearly equal the best to-day. When the period is short, however, the magnet must be strong, and if the sensitiveness is at the same time to be great, the coil must be small as well. Normal-sensitiveness combined with shortness of period is therefore the real test of the instrument-maker's skill, as it is also the measure of general usefulness, except for ballistic work. If the critical resistance is also high, the test is especially severe.

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[1] The coil was made in this laboratory from wire furnished by the Leeds and Northrup Company. In winding the coil, the most scrupulous cleanliness was observed in every respect and the work was done in a room far removed from the machine-shop.

Dust and dirt, which nearly always contain traces of iron, are known to be fatal to the magnetic purity of galvanometer coils. It is important to note that an excellent coil may be ruined by a very slight amount of careless handling or a few minutes' exposure to a dusty atmosphere.

[2] The suspension was as usual by phosphor-bronze ribbon. This case proves that the set of fine phosphor-bronze suspensions need not cause appreciable zero shift.

## GALVANOMETER POSSIBILITIES.

The following table gives the sensibility attained and the coil resistance needed for various periods and resistances, computed by means of some of the equations given above. The field strength is taken at 1,000 lines, and easily attainable values for $Q$ and $K$ are assumed. The table therefore does not attempt to represent the extreme possibilities of galvanometer construction.

### TABLE II.

*Typical galvanometer performance.*

*Field strength,* 1,000 *lines. Minimum value of* $Q$, .17; *of* $K$, .05.

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Moment of torsion, $Q$. | .17 | | .17 | | .495 | | 1.98 | |
| Moment of inertia, $K$. | .43 | | .05 | | .05 | | .05 | |
| Period, $T$. | 10 | | 3.4 | | 2 | | 1 | |
| Resistance, $R$. | 50 | 500 | 50 | 500 | 50 | 500 | 50 | 500 |
| Voltage sensibility, $V$. | 3.8 | 1.2 | 2.2 | .71 | 1.0 | .32 | .36 | .11 |
| Current sensibility, $S$. | 192 | 610 | 112 | 350 | 50 | 160 | 18 | 57 |
| Coil resistance, $R'$. | 3 | 30 | 8 | 82 | 14 | 140[1] | 28 | 280[1] |

In practice, the effective sensibility can be made greater than here given by increasing the scale distance. In the table, the loss in sensibility when the period is decreased from 10 to 3.4 seconds is only about .3 as much as in the further reduction from 3.4 seconds to 1. This is because the first change is produced by altering the moment of inertia, $K$, while the second involves an increase in the moment of torsion, $Q$. It is always more profitable in point of sensibility to decrease the period by decreasing $K$ than by increasing $Q$. The table in this case illustrates the discussion on page 383, above.

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[1] These values are impossible, since when $K$ is .05 the resistance of an open coil cannot easily be made greater than 100 ohms. The above combinations, therefore, of high resistance and short period require either a stronger field or else an increase in both $K$ and $Q$, with resulting loss of sensibility. On the other hand, for the 10-second period a weaker field would evidently suffice.

*Auxiliary Damping.* — When an auxiliary damper of any kind is added to the coil, the current energy is divided between the main circuit and this damper in proportion to their damping coefficients. If $D'$ is the damping coefficient of the main circuit, $d$ of the frame, and $D = D' + d, = 2\sqrt{KQ}$, the critical damping coefficient, equations (18$a$) and (19$a$) become

$$V^2RQ\frac{1}{T} = 12.6\,\frac{D'}{D} \qquad (18b)$$

$$V^2RK\frac{1}{T^3} = .32\,\frac{D'}{D} \qquad (19b)$$

Equation (20$b$) may be treated as follows:

For critical damping $2\sqrt{Q(K+k)} = D' + d$,

or

$$\frac{4\pi(K+k)}{T} = \frac{G^2}{R} + \frac{g^2}{r'} \qquad (23)$$

where the small letters apply to the frame.

Hence

$$\frac{K+k}{T} = H^2\frac{R'}{R}\frac{K}{A^2} + \frac{H^2}{a^2}\frac{r'}{r'}k = H^2\left(\frac{R'}{R}\frac{K}{A^2} + \frac{k}{a^2}\right)$$

$$= H^2\frac{R'}{RA^2}\left(K + k\frac{A^2}{a^2}\frac{R}{R'}\right). \qquad (24)$$

But

$$\frac{D'}{d} = \frac{\dfrac{G^2}{R}}{\dfrac{g^2}{r'}} = \frac{\dfrac{H^2R'K}{A^2R}}{\dfrac{H^2r'k}{a^2r'}} = \frac{K}{k}\frac{R'}{R}\frac{a^2}{A^2}$$

(24) thus becomes:

$$\frac{1}{T} = \frac{H^2R'}{RA^2}\left[\frac{K + \dfrac{d}{D'}K}{K + K\dfrac{d}{D'}\dfrac{R'}{R}\dfrac{a^2}{A^2}}\right] = \frac{H^2}{A^2}\frac{R'}{R}\left[\frac{D'+d}{D' + \dfrac{R'}{R}\dfrac{a^2}{A^2}d}\right],$$

whence

$$H = A\sqrt{\frac{R}{R'T}}\sqrt{\frac{D' + d\dfrac{R'}{R}\dfrac{a^2}{A^2}}{D' + d}}. \qquad (20b)$$

$$\frac{a^2}{A^2} = \frac{1}{n}$$

approximately, unless $K'$ is large.

Since there is always some air damping, equations (18*b*) and (19*b*) should in strictness be used instead of (18*a*) and (19*a*), but for practical purposes this is seldom necessary.

The loss in sensibility from energy wasted in dampers is in general not serious. Even when the circuit furnishes only one-fourth of the damping, the sensibility is still half the maximum. On the other hand, the auxiliary damping does not alter with the external resistance, so that in work where changes in the circuit resistance are necessarily frequent a large amount of auxiliary damping may yield an advantage far outweighing the loss in sensibility which it entails. The galvanometer with auxiliary damper will also come to rest on open circuit, which is often a great convenience. If, however, constant galvanometer sensibility is needed, constant resistance must be provided for, and in that case the auxiliary damper loses its main advantage.

With an auxiliary damper and critical damping the period may be made somewhat shorter for the same magnet strength than where the coil is damped wholly by the circuit. This gain is due merely to the fact that the value of $A\sqrt{R}/R'$ is less for the damping frame than for the coil. The resulting period has therefore a lower limit in the period characteristic of the frame alone, and cannot even be brought very near that limit unless the amount of auxiliary damping is large.

The actual shortening in period increases with the amount of damping and with $R/R'$. With $R/R'$ very large, it is proportional to $D/D'$. For air or oil damping the same figures can be approached, even when $R/R'$ is not very large.

*Galvanometer Calculations.* — On account of the simplicity of the principal equations, the purchaser or occasional user of a galvanometer may readily secure the advantages of computation in adapting his instruments to their work. Equations (18*a*), (1) and (20) can obviously be worked backward, that is, from the published or observed values of sensibility, period, etc., the fundamental constants

$$Q,\ K,\ \frac{H\sqrt{R'}}{A}$$

are easily found. With a knowledge of the possibilities of the instrument as determined by the values of these three constants, the best obtainable combination of sensibility, period and resistance can be decided upon.

*The Measurement of Field Strength.* — By means of equation (20), the field strength of a galvanometer can be found by measurements of time and resistance alone; that is, without knowing the size of wire in the coil, the number of turns or the moment of inertia; indeed, without touching the coil at all. For this purpose it is well to know the value of $A$ more accurately. To attain this result, equation (16) may be rederived, taking account of the dead wire and other inert material in the coil. $l$ is the vertical wire in the coil. Let $h$ be the total length of vertical wire actually passing through the field, and $b$, the total length of horizontal wire. Let $K'$ be the moment of inertia of the mirror and other coil fittings. Let $w$ be the product of the resistance per unit length of the bare wire by the mass per unit length, $m$. This is constant for any material, and for copper equals .0000145. Let $n$ be the ratio of the insulated and varnished wire to the bare wire. Then

[1]
$$G = Hhr; \quad K = nm\left(l + \frac{b}{3}\right)r^2 + K' \quad R' = \frac{(l+b)nw}{m}.$$

Eliminating $m$ and $r$

$$G^2 = \frac{H^2R'}{w}\,\frac{h^2}{(l+b)(l+b/3)}\,\frac{K-K'}{n}. \tag{25}$$

Eliminating $G^2$ by (13) and (5), and $Q$ by (1), and giving $w$ its numerical value for copper, we get:

$$H = 425\sqrt{\frac{(l+b)(l+b/3)}{h^2}\,n\,\frac{1}{1-K/K'}}\sqrt{\frac{R}{R'T}} \tag{20c}$$

whence

$$A = 425\sqrt{\frac{(l+b)(l+b/3)}{h^2}\,n\,\frac{1}{1-K'/K}}$$

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[1] These values rather than the simplified ones should be used in designing coils.

*A* is thus the product of four factors; one is constant, the other three enter by their square roots, so that any uncertainty in their values has only half its proportional effect on the result. The second factor depends on the dimensions of the coil and field, and can be easily calculated. It will, moreover, be practically constant for the same instrument, and will seldom vary over 20 per cent. $K'/K$ will be small, and $K'$ can be estimated from the dimensions and known density of the coil fittings, which will usually be of brass or glass. The second factor, $n$, is more uncertain. It will ordinarily vary from 1.4 to 1.6, and will be somewhat less for larger sizes of wire. In a coil 2 × 5 cm., wound with 2 mil. wire (.005 cm. diameter) *A* was approximately 750. Sixty-two per cent. of the wire passed through the field. In general, *A* will vary between 600 and 800, depending mainly on the width of the coil, and with coils of the usual dimensions it will vary approximately 10 per cent. for a change of 50 per cent. in coil width. The error in determining field strength by application of equation (20*b*) will seldom exceed 10 per cent.

*Adjustments.* — When a galvanometer is to be used for any length of time on one piece of work, an hour or so is usually well spent in adjusting it for the most effective service. In such cases a convenient procedure is as follows: The instrument is set up, with all damping frames removed, in series with a resistance box and connected to a suitable source of electromotive force, such as a potentiometer. The critical resistance and the corresponding sensibility are then determined. This can be done within 2 or 3 per cent., since a resistance which is 10 per cent. too great or too small produces a noticeable effect upon the damping. The internal resistance is also found, and hence, approximately, that of the coil. The period is also observed. The data thus obtained determine completely the possibilities of the instrument; the most satisfactory adjustment can readily be computed and made in the quickest way. For this the following equations may be used:

$$\begin{aligned} T^2 &\propto \frac{K}{Q} \\ V &\propto \frac{G}{QR} = \frac{Hlr}{QR} \qquad (26) \\ G^4 &\propto R^2QK, \text{ for critical damping.} \end{aligned}$$

If we regard the coil as a fixed part of the instrument, the changes which can be made, in the order of their ease, are:

1. The total resistance, $R$, can be altered.
2. The field strength, $H$, can be decreased, if the instrument is provided with a magnetic shunt.
3. The moment of inertia, $K$, can usually be increased by hanging a mass from the coil.
4. A damping frame can usually be attached to the coil.
5. The moment of torsion, $Q$, of the suspending wire can be altered, by substituting a new wire or by shortening the one in place.

Any single change will of course spoil the adjustment for critical damping, hence at least two changes must be made for any new adjustment.

The above changes permit the following adjustments:

1. It is desirable to increase the resistance $R$, $N$ times.

| Compensating Change. | Change in V. | Change in T. |
|---|---|---|
| (*a*) add a damper. | dim. $N$ times. | increases. |
| (*b*) dim. $Q$ $N^2$ times. | inc. $N$ times. | increases $N$ times. |
| (*ab*) dim. $Q$ $N$ times, add damper. | none. | increases. |

2. The sensibility, $V$, is to be increased $N$ times.

| Changes to effect this. | | Change in T. |
|---|---|---|
| (*b*) dim. $Q$ $N^2$ times. | Inc. $R$ $N$ times. | Increases $N$ times |
| (*c*) dim. $R$ $N$ times. | Inc. $K$ $N^2$ times. | Increases $N$ times. |
| (*bc*) dim. $Q$ $N$ times. | Inc. $K$ $N$ times. | Increases $N$ times. |
| (*d*) dim. $R$ $N^2$ times. | Dim. $H$ $N$ times. | no change. |

3. The period, $T$, is to be increased $N$ times.

| Changes to effect this. | | Change in V. |
|---|---|---|
| (*e*) inc. $Q$ $N^2$ times. | dim. $R$ $N$ times. | diminishes $N$ times. |
| (*f*) inc. $Q$ $N^2$ times. | add a damper. | diminishes $N^2$ times. |

## NOTES.

(*a*) The increase of period will be due to the weight of the damper and its amount will depend on the amount of change to be made; that is, on the value of $N$, and also on the value of $R/R'$. A large value of $R/R'$ and a small value of $N$ are the conditions most advantageous for the damper. See equation (26 *b*).

(*ab*) Any other desired combinations of *a* and *b* can of course be made as readily as this particular one. In general, adjustments involving a change in $Q$ are not likely to come exactly right the first time. It will usually be preferable to make the final and more exact adjustment, where this is needed, in some other way, as, for instance, to alter the scale distance in order to change slightly the effective sensibility.

(*f*) On account of the weight of the damper, the decrease in the period is less than with (*e*). The method in (*f*) would be preferable where the resistance could not be diminished.

A damping frame can usually be adjusted by trial about as quickly as by calculation.

It is of course possible to decrease the period and increase the sensibility at the same time by making a large decrease in the resistance, but the resulting gain is so small as seldom to be worth while.

*Ballistic Efficiency.* — The advantages for ballistic work of a damped galvanometer, and therefore of the moving coil galvanometer, are sufficiently well known.[1] If $S_B$ is the ballistic sensibility (in scale divisions per microcoulomb),

$$S_B = S\frac{2\pi}{TX} \tag{27}$$

where $X$ depends upon the damping, and for critical damping equals $e$, the Napierian base. This equation involves, as usual, the assumption that the discharge passes before the coil has had time to move appreciably. In many cases the error due to this assumption is not negligible, and a correction for the time of discharge is applied.[2]

Equation 27 indicates that for closed circuit work the best construction for the ballistic galvanometer is ordinarily the same as for the constant current galvanometer of equal period. The period of the ballistic galvanometer, however, must in general be longer than with the direct current instrument, to permit of accurate reading. When the deflection occurs on open circuit, as in discharging condensers, there is no coil damping, and the sensibility can without inconvenience be increased very considerably by using a strong field. A high resistance may then be inserted, sufficient to give critical damping if the coil is brought to rest by closing the circuit. A galvanometer thus made sensitive may therefore be treated as a critically damped instrument of very high resistance.

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[1] H. Diesselhorst, Drud. Ann., 9, 458, 1902. O. M. Stewart, PHYS. REV., 16, 158, 1903.

[2] E. Dorn, Wied. Ann., 17, 654, 1882; H. Diesselhorst, Drud. Ann., 9, 712, 1903; F. Kohlrausch, Lehrb. der Prak. Phys., 10th ed., p. 480.

The sensibility of a critically damped ballistic galvanometer, for the same control, can also be increased in another way, which applies to both closed and open circuits, namely, by diminishing the period. The ballistic, unlike the steady current galvanometer, does not when critically damped utilize any definite fraction of the available electrical energy. The physical reason for this is found in the fact that the energy taken up by the coil depends in part upon the distance it rotates while the impulse is acting upon it, and this distance obviously increases as the coil becomes smaller.

The sensibility cannot be increased indefinitely by either of these methods, since that would involve getting an infinite amount of work from a finite amount of energy. When the field strength of the steady current moving coil galvanometer is indefinitely increased, the sensibility also increases and with it the energy stored up during deflection; but the instrument becomes overdamped; that is, it demands a longer time and therefore more electrical energy, in order to produce that deflection. With the ballistic galvanometer the energy cannot be increased, and therefore the deflection must ultimately reach a limit, no matter how short the period or how strong the field. How this limit occurs can perhaps be best seen by finding an expression for the energy. The total electrical energy, in absolute units, equals

$$\frac{1}{R}\int_0^\tau E^2dt = \frac{E_1^2\tau}{R}$$

where $E$ is the instantaneous E.M.F. and $\tau$, the duration of the impulsive discharge.

The energy taken up by the coil may be found as follows: Assuming that $\tau$ is very small — the assumption involved in equation 27 — the velocity of the coil at the end of the impulsive discharge is:

$$\frac{G\int_0^\tau Edt}{RK}, \quad = \frac{GE_2\tau}{RK}.$$

The energy is: $G^2E_2^2\tau^2/2R^2K.$

Putting in, for simplicity, the condition of critical damping, $G^2/2R = \sqrt{KQ}$, this becomes:

$$\frac{E_2^2\tau^2}{R}\sqrt{\frac{Q}{K}}, = \frac{E_2^2}{R}\,\frac{2\pi\tau^2}{T}.$$

The fraction of the total energy taken up by the coil is therefore:

$$\frac{\dfrac{E_2^2}{R}\,\dfrac{2\pi\tau^2}{T}}{\dfrac{E_1^2\tau}{R}}, = \frac{E_2^2}{E_1^2}\,\frac{2\pi\tau}{T}.$$

$E_2^2/E_1^2$ will vary from ½ to 1, depending on the wave form of the impulsive discharge. If $\tau/T$ is small, the critically damped ballistic galvanometer is very inefficient, and its sensibility can be increased without difficulty, by diminishing its period or otherwise. This is, of course, the usual case. As $\tau/T$ increases, the instrument will use a larger fraction of the available electrical energy. In this case, therefore, the deflection will approach its limit for a given value of $Q$; but in this case, also, the fundamental assumption of equation 27 no longer holds, and the correction for the time of discharge increases. It is the increase of this correction as $T$ grows smaller which furnishes the needed limiting condition to the increase of sensibility.

With a condenser discharge the case is slightly different, for there the discharge itself is also protracted by the reaction of the moving coil.

## SUMMARY AND CONCLUSIONS.

I. All galvanometers when critically damped by the coil alone are subject to three conditions.

The first of these is that the galvanometer during deflection utilizes nearly 16 per cent. of the energy of the steady current, $I^2RT$. The second is the well known relation between moment of inertia, moment of torsion and periodic time. These conditions lead to the familiar relations between sensibility, period, resistance and controlling force.

The third is the well-known condition for critical damping. For the moving coil galvanometer this condition may be expressed in a new and convenient form as a relation between the periodic time and the field strength, modified by the ratio between external and internal resistance, and also to a slight extent by the form of coil. The period, therefore, is practically determined by the field strength, no matter what the sensibility may be.

II. To the three generally recognized points of excellence in moving coil galvanometers it therefore seems desirable to add a fourth. The four points then are:

1. *Steadiness of the Coil.* — This depends upon accuracy of construction, but more upon the conditions under which the instrument is used.

2. *Smallness of Controlling Force.* — This depends upon delicacy of construction. It is an advantage which may be variously used to secure large sensibility, high resistance, or shortness of period.

3. *Ability to Secure Short Period.* — This depends essentially upon field strength. Whether a short period is consistent with a given sensibility, etc., depends upon the delicacy of construction. The question here is of the ability to secure the short period at all in a critically damped instrument.

4. *Constancy of Zero.* — This is wholly a question of magnetic action. It depends upon the shape of the field and the width and magnetic purity of the coil. It also increases as the period becomes shorter and the coil resistance greater.

III. The advantages of light coils are often insufficiently appreciated.

IV. High normal-sensibility, combined with shortness of period, is the real test of skill in galvanometer construction.

V. A high total (critical) resistance increases the difficulty of securing these advantages.

VI. Auxiliary dampers diminish sensibility, but have certain obvious advantages. Under some conditions they diminish the possible period more than they do the sensibility. This action may be greater with air and oil than with magnetic dampers.

VII. It is possible to determine within 10 per cent. the field strength of a galvanometer by measurements of time, sensibility and resistance, combined with inspection of the coil.

VIII. Nearly all that is practically important in the theory of moving coil galvanometers can be included in three short equations between quantities which can easily be determined for most instruments. Computation, therefore, can be easily and advantageously employed in adapting a galvanometer to any particular task.

IX. The ballistic galvanometer, as usually employed, with an impulsive discharge of very short duration, is very inefficient. The quantity of electricity required to produce a given deflection is of the same order of magnitude as with the steady current instrument, but the energy is far greater. As the time of the discharge approaches the periodic time of the galvanometer, the efficiency increases.

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WASHINGTON, D.C., May 29, 1906.

# ON PRECISION MEASUREMENTS WITH THE MOVING COIL BALLISTIC GALVANOMETER.

By Anthony Zeleny.

THE moving coil ballistic galvanometer possesses an important advantage over the stationary coil type in that it is free from ordinary external magnetic disturbances, but it presents a number of difficulties for work of high precision. It is the object of this paper to show how these difficulties may be overcome so that measurements with this galvanometer can be made to as high a degree of accuracy as is attainable with direct deflection methods. The various details, many of which are well known and are included only for the purpose of completeness, will be considered under the following subdivisions.

§ 1. Set in the fiber, hysteresis, and zero or null point readings.
  (*a*) In ballistic work.
  (*b*) With continuous currents.
  (*c*) Choice of suspension fiber.
§ 2. Damping on closed circuit.
§ 3. Adjustment for equal deflections. Circular scale.
  Increase of period. Shunting of galvanometer.
§ 4. Methods of bringing the coil to rest.
  (*a*) In open circuit work.
  (*b*) In closed circuit work.
§ 5. Throws from a vibrating coil.
§ 6. The variation of the constant. The damping factor.
§ 7. Methods of determining the constant.
  (*a*) The figure of merit and period of vibration method.
  (*b*) The earth inductor method.
  (*c*) The standard solenoid method.
  (*d*) The standard condenser method.
§ 8. The standard mutual inductance coil.

§ 9. Correction for thermo-electric currents.
  (*a*) Changing from closed to open circuit.
  (*b*) Changing from open to closed circuit.
§ 10. Galvanometer resistance by a method of damping.
§ 11. Conclusion.

## §1. SET IN THE FIBER, "HYSTERESIS," AND ZERO OR NULL POINT READINGS.

When a set is "given to a fiber" during an observation, so that the coil does not return to its original position, the error due to it may be avoided in the following manner:

(*a*) *In Ballistic Work.* — A throw that is at least equal to the maximum to be used is given to the coil, so that a set is affected in the direction of the throws which are to follow. The coil on returning to the null point must not be allowed to move past it (see §4), as otherwise a part of the set is removed.[1] Subsequent throws in the same direction cause little or no additional set. It rarely happens that an additional set is given, and if any is observed the throw producing it must be discarded.

(*b*) *With Continuous Currents.* — The correction for the set is avoided in the same way as in ballistic work. To note the amount of the set the coil must here also be brought aperiodically to the null point. The null reading observed after the deflection and not the original one, if it differs from it, must be employed in the calculation of the deflection.

In comparing currents which are not of approximately the same strength regard must be taken for an apparent "hysteresis" which exists in many if not all moving coil galvanometers. The same current produces a different deflection depending on whether it has increased from zero or decreased from a larger value. The observations of Table I. indicate the amount of this variation in the case of two galvanometers. The null point after the larger reading remained the same as that after the lesser one in each case. Different currents were used in the three cases given, so as to make the deflections in all of them about the same.

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[1] In most galvanometers the coil can move beyond the null point an amount equivalent to two or three centimeters on the scale without producing an appreciable effect on the set or the magnetic hysteresis of the coil.

TABLE I.

| Galvanometer. | Suspension. | Deflection in Cm. Current Increased from Null Reading. | Deflection in Cm. Current Decreased from Twice Its Value. | Variation. |
|---|---|---|---|---|
| An open coil type. (Leeds & Northrup "H" Type.) | Phosphor-bronze. | 10.91 | 11.00 | 0.8 % |
| | Steel. | 12.64 | 12.69 | 0.4 % |
| A cylindrical coil type. (Made in the laboratory. Coil of special "iron free" wire on wooden spool.) | Phosphor-bronze. | 10.42 | 10.68 | 2.0 % |

These variations are not due to changes produced by the larger current heating the fiber, for the deflection taken again from the null position is the same as it was in the first case. They are probably due to changes in the direction of magnetization of the magnetic impurities within the coil.

Whatever may be the cause of this hysteresis observed when employing continuous currents, it is probable that ballistic throws of unequal magnitude are not proportionally affected by it. This hysteresis even affects throws of equal magnitude. After some period of rest the first throw differs from the following ones obtained for the same quantity by an amount usually exceeding 0.2 per cent. and therefore should always be discarded.

(*c*) *Choice of Suspension Fiber.* —It is desirable to choose the suspension fiber[1] which gives the least amount of set after reversal of deflection. A phosphor-bronze strip that gives a set of several millimeters can often be replaced by a phospor-bronze wire, a coarser strip or a steel fiber giving much less set. In each case, however, this is accomplished at the expense of sensitiveness, as shown in Table II., so that in many cases the 1.5 mil phosphor-bronze strip is selected. In the observations given in Table II., the lower suspension was the same phosphor-bronze spiral in each case, the upper suspension only being changed.

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[1] W. E. Ayrton, Phil. Mag., 1890, Vol. 30, p. 58; Electrical World, 1892, Vol. 19, p. 178.

TABLE II.

| Upper Suspensions of Equal Length. | Sensibility in "Megohms." | Time of Double Vibration on Open Circuit. | Ballistic Throw for Equal Quantities. | Set in Fiber on Reversal After Full Scale Deflection of 25 Cm. = 14°. |
|---|---|---|---|---|
| 1.5 mil phosphor-bronze strip. | 252.0 | 17.88 sec. | 9.03 cm. | 0.27 cm. |
| 1.5 mil phosphor-bronze wire. | 109.6 | 12.00 " | 5.80 " | 0.06 " |
| 3 mil phosphor-bronze strip. | 47.8 | 7.80 " | 3.77 " | 0.04 " |
| A steel strip. | 23.1 | 5.44 " | 2.60 " | 0.00 " |

## § 2. DAMPING ON CLOSED CIRCUIT.

The value of the damping factor on open circuit is usually about 1.02, but on closed circuit it is greatly increased and so diminishes[1] the sensitiveness of the galvanometer. Fig. 1 gives an experi-

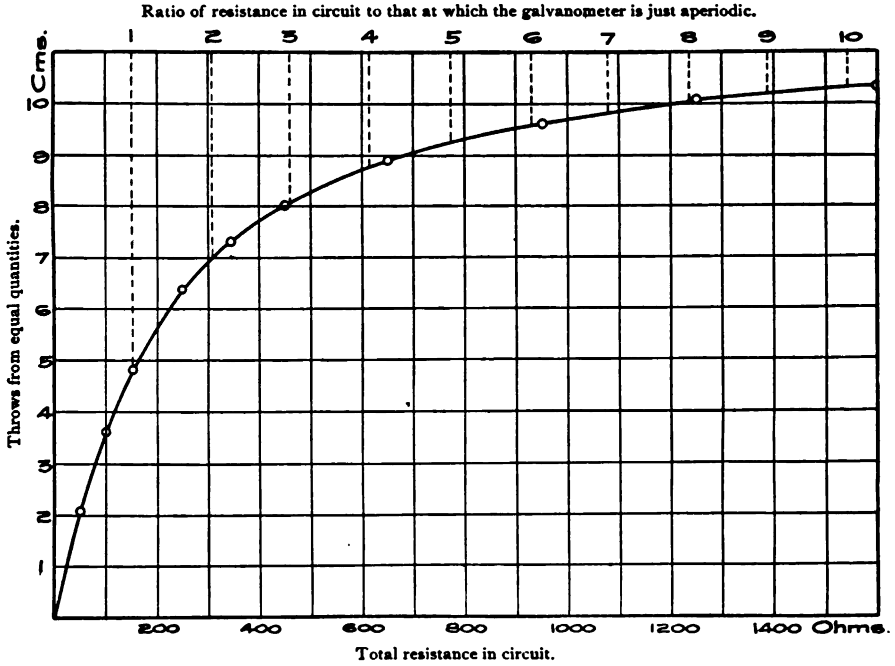

Fig. 1.

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[1] H. Diesselhorst, Annalen der Physik, 1902, Vol. 9, p. 458.

mental curve showing the relation between the resistance in the circuit and the throws produced on a circular scale by equal quantities of electricity. The resistance of the galvanometer coil was 54 ohms, and its motion was just aperiodic when the total resistance in the circuit was 154 ohms. This curve applies to all galvanometers when the abscissas are plotted in terms of the ratios of the resistance in the circuit to the resistance at which the galvanometer is just aperiodic.

If the field of the magnet is uniform (and radial) the damping with the same resistance is constant for throws of all magnitudes,[1] but as this condition is never fully realized (see § 6), the damping factor is only approximately the same. Since its value is much greater on closed than on open circuit work the proportionality of the throws is more affected [2] in the former than in the latter case. For this reason and on account of the greater sensitiveness it is preferable whenever practicable to employ the galvanometer on open circuit.

## §3. ADJUSTMENT FOR EQUAL DEFLECTIONS, CIRCULAR SCALE, INCREASE OF PERIOD, SHUNTING OF GALVANOMETER.

When the plane of the coil is parallel to the magnetic lines of force the deflections for the same continuous current should be equal in the two directions. This condition is the most desirable one for ballistic work also and can be obtained only by trial. Two short pointers [3] are attached, one to the coil and the other to a stationary part of the galvanometer. When the adjustment for equal deflections is completed the stationary pointer is bent until the tips of the two are in line. Future adjustments of the instrument can then be made with ease. These pointers are of special service for placing the coil on successive adjustments into the same part of the field to maintain the sensitiveness unchanged.

A circular scale of a radius equal to its distance from the axis of suspension of the coil is much to be preferred for accurate work because the telescope is then in focus for all parts of the scale and the usual parallax is avoided. For ballistic throws the necessity of changing scale readings to angular measure or to equivalent[1] circular scale readings is also avoided.

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[1] O. M. Stewart, PHYS. REV., 1903, Vol. 16, p. 158.

[2] Donegan and Smith, Electrical Engineer, 1903, p. 830, have shown experimentally the presence on closed circuit of large variations in damping for throws of different magnitude.

[3] The Leeds and Northrup Company, at the suggestion of the writer, have already added these pointers to some of their galvanometers.

A convenient way of changing the period of the galvanometer without changing the fiber or the coil is as follows: A brass wire with two lead balls attached to its extremities is bent in such a manner as to clamp easily onto the lower end of the coil. The moment of inertia of the system can be changed readily by bending the wire so as to alter the distance between the lead balls. Any desired period can be attained in this manner.[2]

In this type of galvanometers the constant is changed after an abnormally large deflection (see § 6). For this reason where large currents are liable to enter as in experiments requiring the balancing of the wheatstone bridge the shunting of the galvanometer must be made with special care while the balancing is in progress.

## § 4. METHODS OF BRINGING THE COIL TO REST.

As shown in § 1, the coil must return to the null position without crossing it more than a small amount. This is accomplished in the following manner:

(*a*) *In Open Circuit Work.* — If the galvanometer is aperiodic on closed circuit the coil is short-circuited after the throw at some point on its return, depending on the amount of damping present. If this is made at the proper place the coil reaches the null reading in the least possible time. Sometimes it is more convenient to close and open the circuit several times while the coil is in motion.

When the coil is finally at rest on the closed circuit, it is usually not at its true null point. A thermo-electric current existing in the circuit is deflecting the coil so that when the circuit is opened a vibration of several millimeters may occur. This is checked by quickly tapping the short-circuiting key while the coil is passing through the null point from the deflected position. In some cases this is better accomplished by tapping several times while the coil is moving to the null point and checking the motion a little at a time, as in the case above.

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[1] Kohlrausch, Physical Measurements, 1894, p. 446.

[2] Since the writing of this paper a galvanometer made by Hartmann and Braun has been described in Biddle's Bulletin, Sept., 1906, which has attached to a pillar at the lower end of the coil a cross arm carrying at either end a small pan. Weights placed into these pans alter the moment of inertia of the system.

If the galvanometer is not aperiodic on closed circuit the usual inductance coil is introduced and the motion checked by the movement of a magnet within this coil. To avoid the motion due to the thermo-electric currents the writer has for some years introduced a thermo-electric couple into the galvanometer circuit in addition to the inductance coil. By means of this the galvanometer is brought to the true null point before the circuit is opened. The thermo-electric couple suited for this purpose is one of brass wire, having the temper of a portion changed by heating to white heat. This portion forms a thermo-electric element with the remainder of the brass, so that by holding one's fingers on one side or the other it gives the proper thermo-electromotive force to overcome that in the circuit. Changing the pressure of the fingers upon the junction alters the thermo-electromotive force within the proper limits. Some, including the writer, prefer to use the inductance coil for this adjustment also, although it may require longer practice to attain ease in manipulation.

(*b*) *In Closed Circuit Work.* — On closed circuit work the best condition exists when the galvanometer is just aperiodic, requiring no attention to bring the coil properly to the null point. If the coil is over-damped a resistance can be temporarily introduced to lessen the damping. It must be removed, however, before the final reading is taken, as it alters the thermo-electric current in the circuit, causing a change in the null reading which in this case must be taken while the circuit is closed. If the coil is not damped sufficiently the inductance coil and magnet method must be employed as in part (*a*) above.

## § 5. THROWS FROM A VIBRATING COIL.

When a ballistic throw is to be taken while the coil is not entirely at rest the discharge must be made when the coil is at either turning point of its motion. The throw in either case must be computed from the natural null point and not from the point at which the throw originated as is sometimes stated. This is true for vibrations small in relation to the throws and not for large ones. These vibrations need never exceed .02 or .03 cm. The writer, in his own work, never allows more than .01 cm. Table III. gives the throws obtained for the same quantity when discharged while the coil is at rest and again when at each of the extremes of its motion which was 0.3 cm., to either side of the null point and is greater than should be tolerated in practice. The larger variations in the throws of the last column are due to the inability of causing a throw at the exact time of the greatest elongation. The average values, however, agree with the deflection (column 1) made from the true null point. If the amount of vibration to each side of the null point exceeds 3 per cent. of the total throw an appreciable variation from the above condition is observed.

Table III.

| Coil at Rest at 25.00 Cm. | Vibrating Coil at Elongation. 25.30 Cm. | Vibrating Coil at Elongation. 24.70 Cm. |
|---|---|---|
| 35.53 | 35.53 | 35.52 |
| 35.52 | 35.53 | 35.52 |
| 35.52 | 35.52 | 35.54 |
| 35.53 | 35.52 | 35.51 |
| 35.525 | 35.525 | 35.523 |
| 25.00 | 25.00 | 25.00 |
| 10.525 | 10.525 | 10.523 |

## § 6. The Variation of the Constant — The Damping Factor.

It is well known that the strength of the magnetic field and the torsional moment of the suspending fiber change[1] with temperature and the moment due to the same impulse alters slightly on account of the expansion of the copper coil. Variations in the constant, however, are liable to occur during a single experiment even though the temperature remains constant. The observations given in Table IV. represent the magnitude of the throws produced by the same quantity of electricity at four different intervals during the same experiment. Between the sets of observations, however, the galvanometer coil had received deflections much larger than the throws employed. These deflections produced an apparently permanent change in the constant of the galvanometer. This is probably due mainly to a change in the direction of magnetization of the magnetic impurities in the coil as in the case of set and hysteresis considered in § 1.

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[1] B. O. Pierce, Am. Acad. Proc., 1893, 38, p. 551.

TABLE IV.

| Temperature °C. | Throws in Cm. | Change in Cm. | Change in Per Cent. |
|---|---|---|---|
| 20.2 | 19.908 ± 3 | —— | —— |
| 20.3 | 19.893 ± 3 | −.015 | 0.07 |
| 20.3 | 19.824 ± 3 | −.084 | 0.42 |
| 20.2 | 19.445 ± 3 | −.463 | 2.28 |

These changes render it impracticable for work of precision to assume that the constant of the galvanometer which is used for various deflections remains unchanged for any considerable length of time. Constancy can be assumed however for consecutive throws of the same magnitude providing that in the mean time no set has been given to the fiber and that the instrument has not been jarred or the temperature of the room changed.

The damping factor[1] $\sqrt{\theta_1/\theta_2}$ as mentioned in § 2 changes somewhat with the amount of throw, very little in a galvanometer of a nearly uniform (radial) field and a considerable amount in some galvanometers. In one galvanometer used by the writer the damping factor on open circuit for throws of

$$15.6 \text{ cm.} = 1.0243 \pm 1$$

and for

$$4.0 \text{ cm.} = 1.0193 \pm 3,$$

a variation of 0.5 per cent. In some galvanometers this variation was found to be as small as 0.2 per cent. but usually it is larger. This shows that if throws of unequal size are to be compared a correction must be made for the variation in the damping. This correction for large throws is somewhat uncertain because the amount of set in the fiber changes in the consecutive unequal vibrations to the opposite sides of the null point. It is therefore desirable whenever practicable to make the quantities compared nearly equal rendering this correction unnecessary and avoiding the usual requirement of an accurate adjustment of the scale with respect to the normal to the mirror.

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[1] The simplicity of this form makes it preferable to the logarithmic decrement still commonly employed. This simpler form is explained by Stratton and Milliken, Experiments in General Physics, 1896, p. 86; Zeleny and Erikson, Manual of Physical Measurements, 1902, p. 102; A. W. Smith, PHYS. REV., 1906, Vol. 22, p. 250.

## § 7. METHODS OF DETERMINING THE CONSTANT.

Since in this type of galvanometers, as was shown in § 6, the constant varies and must therefore be redetermined frequently, it is especially desirable that the method employed for its determination should be one which for the same degree of accuracy requires the least time. The four usual methods[1] are considered separately.

(*a*) The "Figure of Merit and Period of Vibration Method" can be employed in open circuit work only and usually is of little value where an accuracy greater than one half of one per cent. is required. The deflected coil is in a field of a different strength than when in its null position and therefore the figure of merit obtained from a continuous current has a value different from the one required for the ballistic constant. The length of time necessary for a determination of the constant and the uncertainty of the effect of the set in the fiber and of the hysteresis are additional reasons for discarding this method in work of precision.

(*b*) The Earth Inductor Method can be employed for determining the constant on closed circuit and by special construction on open circuit also. The determination of the strength of the magnetic field and of its variation in direction and intensity, especially in modern cities, render this method too difficult if not impracticable for the kind of work under consideration.

(*c*) The Standard Solenoid Method is the most practical of the three direct methods. The constant can be determined on either closed or open circuit and with an accuracy limited only by that with which the constants of the solenoid can be measured. The large size of the coil and the accuracy of construction required for work of the highest precision are its chief objections. (See § 8 and § 9(*a*).)

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[1] Henderson, Practical Electricity and Magnetism, 1898, pp. 211–229.

(*d*) The standard condenser method, although an indirect one, is by far the most convenient of all the known methods. If the capacity[1] (free charge) and the temperature coefficient are accurately known it is capable of the highest attainable precision.

For open circuit work the condenser is charged by means of a standard cell and immediately discharged through the galvanometer, the circuit being opened before a measurable amount of the absorbed charge is liberated. This can be accomplished most conveniently by means of a special key, a Pohl commutator properly arranged as described in a previous paper above referred to, or by means of keys operated by a swinging pendulum. A single tap on an ordinary discharge key will also accomplish the same result with fair accuracy.

To obtain the constant for closed circuit work the condenser is discharged and its circuit opened as in the case above, but in addition, immediately after the discharge, the galvanometer circuit is closed, through the apparatus with which it is to be employed. In this way a known quantity of electricity is discharged through the galvanometer and the latter is damped during the whole[2] of its throw in the same manner as when otherwise employed in that particular circuit.

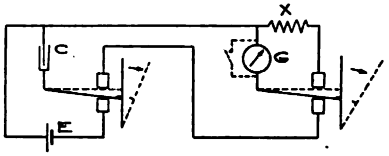

Fig. 2.

The connections are made preferably as shown in Fig. 2. The keys are operated in succession by a swinging pendulum[3] not shown in the figure. The key of Fig. 3 is the same as that already described,[1] with the addition of a contact piece, $S$, which closes the galvanometer circuit through the apparatus $X$ immediately after the opening of the condenser circuit. The Pohl commutator, as shown in Fig. 4, may be employed for the same purpose. The height of the mercury in the cups is adjusted so that the contacts are made or broken in the order indicated by the numerals.

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[1] A. Zeleny, Capacity of Mica Condensers, PHYS. REV., 1906, Vol. 22, p. 65.

[2] When the resistance in the circuit is small the damping is liable to be sufficient so that an appreciable effect on the amount of the throw is produced by the coil moving undamped during the short interval while the condenser is discharging and before the circuit is closed. Care must be taken to make this interval as small as possible. The time of discharge may be made as short as desired by decreasing the capacity of the condenser or the resistance of the galvanometer circuit, or both. The period of the galvanometer may also be increased to reduce the amount of the undamped movement. See also H. Diesselhorst, Annalen der Physik, 1902, Vol. 9, p. 712.

[3] Carhart and Patterson, Physical Measurements, 1900, p. 107.

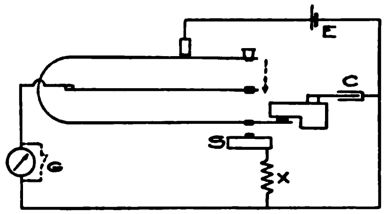

Fig. 3.

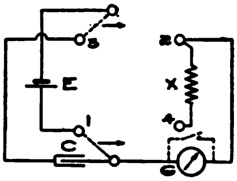

Fig. 4.

In any case the test for proper adjustment is made by varying either the speed of operating the key or the adjustment itself, so as to change the time before the closing of the galvanometer circuit and the time the condenser is allowed to discharge. This variation when made within proper limits should produce no appreciable effect on the throws obtained. If small variations produce an appreciable change the apparatus is not in proper adjustment.

When the circuit is closed an error may be introduced in the result by the thermo-electric current that usually exists in a closed circuit, which itself produces an appreciable deflection. The method of treatment of this is considered in § 9.

The only objection to this method is the uncertainty as to the condenser maintaining the same capacity value from year to year. The condenser plates are held together by the insulating material only, usually paraffin, in which they are imbedded. If the temperature of the room accidentally reaches an abnormally high value, the insulating material may soften sufficiently to allow the plates to change their relative position. For this reason the limiting temperature should be known and the condenser guarded against such extremes as may be known to affect permanent changes.

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[1] A. Zeleny, Phys. Rev., loc. cit.

In the present state of our knowledge of condensers more or less doubt must exist as to their constancy for work of precision. When the condenser has not been exposed to abnormal influences, its capacity is known to remain constant for at least a considerable length of time. This makes it available as a working standard of the highest precision. Under present conditions, however, it must be tested from time to time. Since it is not practicable to send it often to the Bureau of Standards, a method of testing its constancy must be employed which is sufficiently simple to enable the determination to be made with ease and precision in any laboratory. The writer has employed for this purpose what he terms a "Standard Mutual Inductance Coil" (see § 8), which has proved to be very satisfactory.

## 8. THE STANDARD MUTUAL INDUCTANCE COIL.

Two coils are wound one within the other on the same spool of specially well seasoned wood.[1] They are properly insulated and saturated in an insulating compound to prevent any displacement of the wire or any moisture entering the wood. When the coefficient of mutual inductance of these coils is once determined they can be employed in the same manner as a standard solenoid and make a much simpler and cheaper piece of apparatus, capable of at least as high a degree of accuracy.

The coefficient of mutual inductance is determined by comparison with the standard condenser to which it is intended to be a supplement employing the well-known relation[2]

$$Q_s = M\frac{I_p}{R_s}.$$

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[1] Some other material may prove superior to wood. Rosa and Grover, Bulletin No. 3, Vol. 1, Bureau of Standards, have shown serpentine to possess magnetic impurities. Other similar substances must be proved free from them before being employed in standards.

Since the above footnote was written, J. G. Coffin, in the Bulletin of the Bureau of Standards, Vol. 2, p. 89, states that glass and plaster of paris are excellent materials for coils of small size and also gives the advantages of the use of marble. The writer, however, is aware that in at least some grades of marble there are veins of magnetic material.

[2] E. L. Nichols, Lab. Manual of Physics and Applied Electricity, 1894, Vol. 1, p. 243; Zeleny and Erikson, loc. cit., p. 111.

The current $I_p$ in the primary coil is adjusted until the quantity $Q_s$ in the secondary circuit is nearly the same as that given by the standard condenser. On account of the damping on closed circuit (see § 2 and § 9), the secondary circuit is opened by means of a proper key (Figs. 2, 3 or 4 modified), immediately after the passage[1] of the induced charge. When the resistance $R_s$ in the secondary circuit is known the coefficient of mutual inductance $M$ can be calculated and its true value obtained to within 1/100th per cent. This determination should be made before any possible change can occur in the value of the capacity as it had been standardized.

Future comparisons are made by assuming the coefficient of self-inductance to remain unchanged and the coil is used as a standard to determine the quantity discharged from the condenser, from which the value of the capacity is obtained in the usual manner,

$$CE = Q_1 = Kd_1$$

$$\frac{MI_p}{R_s} = Q_2 = Kd_2$$

and

$$C = \frac{d_1}{d_2}\frac{MI_p}{R_s E}.$$

When this value is the same as the original one the constancy of the capacity value is assured. Should any variation be detected it is reasonable to expect that the change occurs in the condenser. To avoid any uncertainty in such a case it is preferable to have two such standards of inductance wound in a different manner on separate spools of unequal diameters. The temperature coefficient of these standards, although very small, should be known or the observations must be taken always at nearly the same temperature.

This Standard Mutual Inductance coil may be used in the same manner as the standard solenoid for the measurement of quantities, in place of the condenser, but possesses the same disadvantage as the standard solenoid in requiring the determination of the value of a current and of a resistance for each observation, which renders it much less convenient for a working standard than the condenser. It is desirable therefore to use it only as a check on the constancy of the condenser.

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[1] The adjustment of the key is readily made on account of the very short time required for the discharge. It has been shown experimentally by E. Rutherford, Trans. New Zealand Institute, 1895, p. 182, that all the measurable part of the induced electricity passes in a few thousandths of a second.

## § 9. Correction for Thermo-Electric Currents.

Electrical circuits containing a galvanometer of the moving coil type are specially liable to thermo-electric currents. These can often be reduced in value and sometimes entirely avoided by screening the galvanometer from heat radiations and from air currents. Since these thermo-electric currents modify the amount of the ballistic throw they should be entirely eliminated. The writer has found the following method of removing them a most satisfactory one:

A secondary circuit $P$ containing the storage cell $E$ and a variable resistance box $R$, also includes a small part $S$ of the galvanometer circuit. This part is composed of a few centimeters of the copper connecting wire. The resistance in $R$ is adjusted until the electromotive force at the extremities of $S$ is equal and opposite to the thermo-electromotive force in the circuit. This condition is tested by closing and opening the key $K$.

When it is not convenient to use this method the following corrections may be employed with a high degree of accuracy.

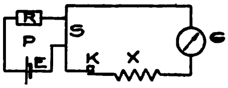

Fig. 5.

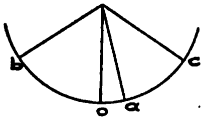

Fig. 6.

(*a*) *When Changing from Closed to Open Circuit.* — This is the most important case as in all closed circuit work it is desirable, as explained in § 2, to open the galvanometer circuit immediately after the discharge to avoid the damping. If the natural null point is at o (Fig. 6), when the circuit is closed, the apparent null point is at $a$ due to the presence of a thermo-electric current. If no thermo-electric current is present a definite quantity of electricity produces a throw $ob = oc$. This same quantity when discharged while the coil is at the apparent null point $a$ produces, when the circuit is opened immediately, an apparent throw of *ab* on one side and *ac* on the other. The throws therefore must be calculated from the true null point, *o*, as it is on open circuit, and not from the apparent one, *a*, observed on closed circuit.

The case is practically the same as that of the throw obtained from the maximum elongation of a vibrating coil as described in § 5.

(*b*) *Changing from Open to Closed Circuit.* — In experiments with the earth inductor and with ballistic galvanometer methods for determining the magnetic properties of iron, it is inconvenient to open the galvanometer circuit before the coil moves an appreciable amount. In such cases it is preferable to determine the constant on closed circuit. If the condenser is employed for this purpose the galvanometer must be closed through the inductance apparatus immediately after the discharge so as to be affected by the proper amount of damping (see § 7, *d*). The throw obtained is influenced by the presence of the continuous thermo-electric current and the result is not the algebraic sum of the maximum effects due to each

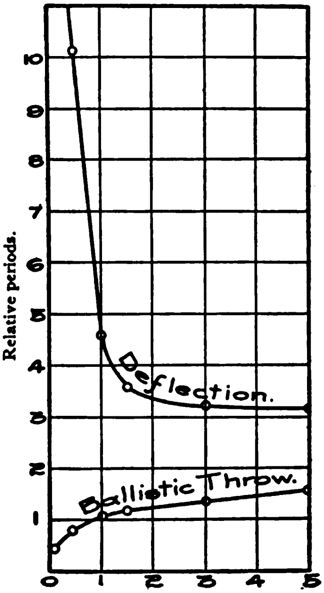

Fig. 7. Ratio of resistance in the circuit to the resistance at which the galvanometer is just aperiodic.

quantity acting alone because the period of the coil is different for continuous currents and for the ballistic throws. The relation of the periods is roughly shown in Fig. 7 for different values of the resistance in the circuit. The value of the correction to be made for the presence of the thermo-electric current depends upon the amount of damping and can be obtained by aid of the curves of Fig. 9 or from the curve of Fig. 10.

The method by which these curves were obtained is as follows:

The data were taken from a Leeds and Northrup open-coil galvanometer of 135 ohms resistance. The suspension was 1.5 mil phosphor bronze strip and the circular scale has a radius of 51.4 cm. The set on reversal from 15 cm. was 0.22 cm. The uniformity of the field on the side that the throws were taken was such as to cause the deflections on a circular scale to be proportional to the current to within 0.1 per cent. The resistance at which the galvanometer is just aperiodic was first determined by the method described by Wenner[1] as shown in the curve of Fig. 8. The curve indicated by the points was extended so as to meet the axis of abscissas. This gives 565 ohms as the resistance at which the galvanometer is just aperiodic and the value is probably correct to within 3 or 4 ohms or about 0.7 per cent.

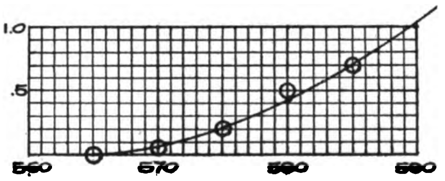

Fig. 8.

The apparatus was then arranged as shown in Fig. 2 with the addition of the secondary circuit described above in this section and shown in Fig. 5. This secondary circuit was employed to cause any desired current in the galvanometer, and for experimental purposes took the place of a thermo-electric current. The keys were adjusted so that the galvanometer circuit was closed in 1/100th second after the beginning of the condenser discharge. The period of the throw on open circuit was 4.8 seconds and on closed circuit, containing the galvanometer only, it was 4.4 seconds.

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[1] Phys. Rev., 1906, Vol. 22, p. 192.

It was shown that for small currents giving a deflection of less than 5 millimeters the value of the correction in per cent. of the total deflection given by the current was numerically the same, near enough for the required purpose, whether the throw was large or small[1] and whatever the direction of the thermo-electric current with respect to the throw. The correction, however, is to be added to or subtracted from the observed throw depending upon whether the electric current is in the opposite or in the same direction as the throw.

It was also shown that for currents giving a deflection of 2 centimeters the correction to be added differed considerably from the one to be subtracted but the average of the two gave the same percentage value as that obtained from the smaller currents. For the purpose of obtaining greater observational accuracy it was considered desirable to use the average correction obtained from the larger currents. The value of the corrections is given in Table V, and plotted in the Curve *B* of Fig. 9. To make the correction applicable to all galvanometers damped in a similar manner the resistance in the circuit is given in terms of the resistance at which the galvanometer is just aperiodic. The total resistance in the circuit is represented by $R_c$ and the resistance at which the galvanometer is just aperiodic by $R_{ap}$.

TABLE V.

| **Resistance Ratio.** $R_c/R_{ap}$. | **Correction in Per Cent. of Thermo-electric Deflection.** | **Resistance Ratio.** $R_c/R_{ap}$. | **Correction in Per Cent. of Thermo-electric Deflection.** |
|---|---|---|---|
| 0.25 | 5.5 | 3 | 57.8 |
| 0.379 | 11.0 | 4 | 65.1 |
| 0.5 | 15.0 | 5 | 69.6 |
| 1 | 27.8 | 7 | 75.8 |
| 1.5 | 39.6 | 10 | 80.6 |
| 2 | 48.1 | | |

In order to simplify as far as possible the method of obtaining the ratio $R_c/R_{ap}$, the following method was employed for obtaining the data for the Curve *A* of Fig. 9, from which the ratio, providing it is greater than unity, can be obtained by means of one observation.

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[1] The magnitude of the throws must be at least three times the deflection produced by the thermo-electric current.

It was first observed that the distance the coil moves beyond the null point after a deflection is proportional to the deflection. It was found that a motion of 3 cm. beyond the null reading produced no appreciable set by the reversal, in the particular galvanometer employed. The deflections used were 20, 10 and 5 cm., depending on the damping in the circuit, the object being to keep the motion beyond the null point as large as possible without exceeding 3 cm. The apparatus was the same as in the case above, but the deflecting currents from the secondary circuits were made larger. This secondary circuit was opened and the distance the coil moved beyond the null point was observed with various resist-

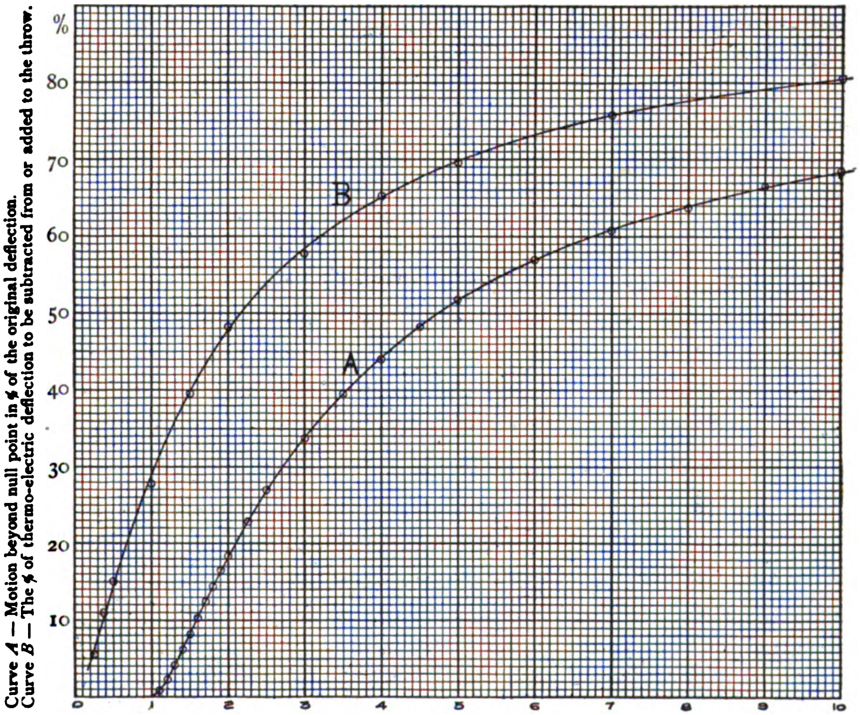

Fig. 9. Ratio of the resistance in the circuit to the resistance at which the galvanometer is just aperiodic.

ances in the galvanometer circuit. The data of Table VI. give the percentage of the original deflection the coil moved beyond the null point for various resistances in the circuit. These also are expressed in terms of the resistance at which the galvanometer is just aperiodic so as to be applicable to any galvanometer.

TABLE VI.

| $R_d/R_{ap}$ | Motion Beyond Null Point in Per Cent. of Original Deflection. | $R_d/R_{ap}$ | Motion Beyond Null Point in Per Cent. of Original Deflection. | $R_d/R_{ap}$ | Motion Beyond Null Point in Per Cent. of Original Deflection. |
|---|---|---|---|---|---|
| 1.01 | 0.02 | 1.7 | 12.49 | 4 | 44.02 |
| 1.05 | 0.35 | 1.8 | 14.45 | 4.5 | 48.10 |
| 1.1 | 0.92 | 1.9 | 16.50 | 5 | 51.85 |
| 1.2 | 2.26 | 2 | 18.43 | 6 | 57.00 |
| 1.3 | 4.05 | 2.25 | 22.93 | 7 | 60.90 |
| 1.4 | 6.10 | 2.5 | 27.00 | 8 | 63.93 |
| 1.5 | 8.15 | 3 | 33.75 | 9 | 66.46 |
| 1.6 | 10.32 | 3.5 | 39.63 | 10 | 68.40 |

If it is desired to find what per cent. of the thermo-electric deflection must be applied as a correction to any ballistic throw, the coil is allowed to return after the throw in its natural way and the distance it moves beyond the null point[1] is observed. The value of this distance in per cent of the observed throw is calculated. From this the value of $R_d/R_{ap}$ is obtained by use of Curve *A*, Fig. 9, and from this value in turn the desired percentage correction by the use of Curve *B*. Since the thermo-electric deflection rarely exceeds 2 mm. an error in the correction of less than 2 per cent. is not appreciable, and it is believed these curves apply to any galvanometer within that limit. The curve of Fig. 10 is derived from the curves of Fig. 9 and gives the values of the percentage correction more directly. Several galvanometers were tested having different resistances and different types of coils, and in each case the correction obtained from the curves agreed with the experimental results.

To illustrate the manner in which the correction is made, suppose a thermo-electric current which gives a permanent deflection of 0.20

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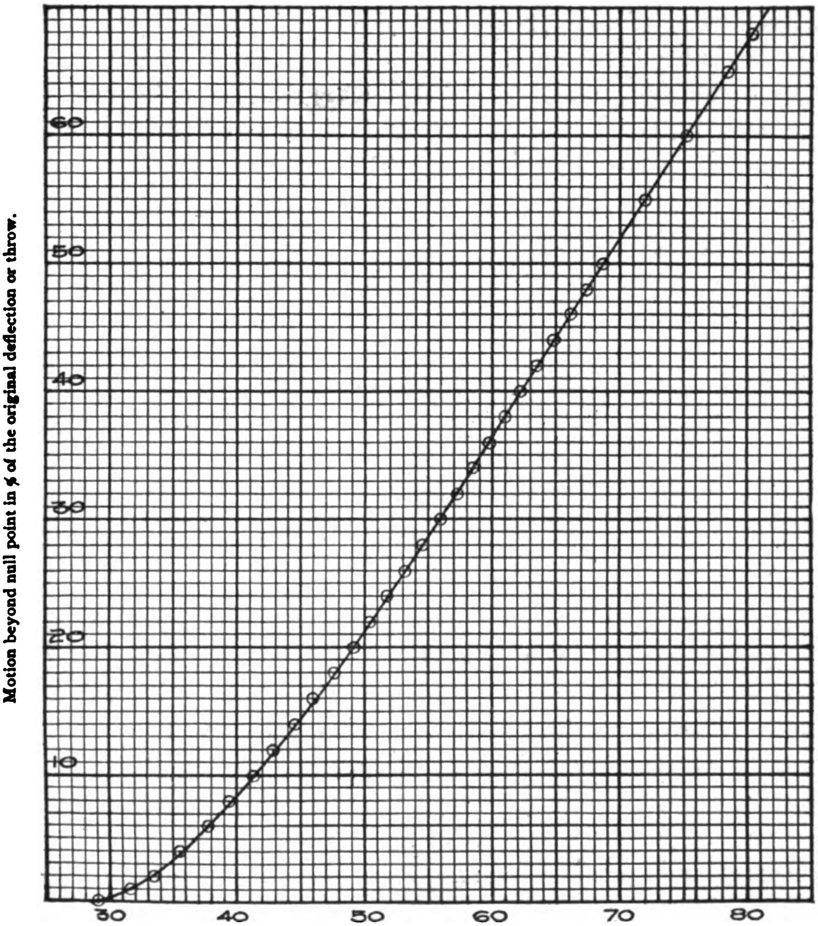
[1] In practice the thermo-electric current alters the null reading on changing from open to closed circuit. This altered null reading must be employed in the calculation of the distance the coil "moves beyond the null point," while the throw itself is calculated from the original null point on open circuit.

cm. when acting alone, and assume the ballistic throw when affected by this thermo-electric current to be 10.00 cm. in the same direction, and that the coil on its return moves 2.7 cm. beyond the apparent null point, *i. e.*, 27.0 per cent. of the observed throw. From Curve *A*, $R_d/R_{ap} = 2.51$, and from this again Curve *B*, gives the value of the correction to be applied as 53.9 per cent. of the deflection produced by the thermo-electric current. The correction, therefore, is 0.11 cm. and in this case is to be subtracted, making



The correction, in % of the thermo-electric deflection, to be added to or subtracted from the throw.

Fig. 10.

the corrected throw = 9.89 cm. From the curve of Fig. 10 the 27.0 per cent. gives the correction of 53.9 per cent. more directly, and this is the curve to be employed in practice.

## § 10. GALVANOMETER RESISTANCE BY A METHOD OF DAMPING.

The Curve *A*, Fig. 9, may also be employed for an approximate determination of the galvanometer resistance.[1] The distance the coil moves beyond the null point is observed on closed circuit, and again with an additional known resistance. If on closed circuit the coil moves *n* per cent. of the original deflection beyond the null point, from Curve *A*, $R_c/R_{ap} = a$. If an additional resistance of *R* ohms causes the distance the coil moves beyond the null point to increase to *m* per cent.,

$$\frac{R_c + R}{R_{ap}} = b.$$

Then

$$\frac{R_c}{R_c + R} = \frac{a}{b},$$

and $R_c$, the resistance of the original galvanometer circuit $= aR/(b - a)$. This is often a very convenient method and gives the resistance with sufficient accuracy for many purposes.

## § 11. CONCLUSION.

The constant of a moving-coil galvanometer is a variable quantity depending on several conditions. For work of the highest precision the unknown quantity must be compared with a known one of nearly equal magnitude and the two throws must be obtained in immediate succession. A set in the fiber must be avoided by always taking the throws in the same direction and stopping the motion of the coil on its return before it crosses the null point. The first throw taken after a period of rest and any throw after which a change in the null reading is observed must be discarded. In the latter case the readings following must not be compared with those taken before. Whenever it is practicable the galvanometer should be used on open circuit. It is then more sensitive and the quantities more nearly proportional to the throws.

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[1] The results obtained for various types of galvanometers by using this method, agree to within 1 per cent. of the true values. On account of the variations in the intensity of the magnetic field being different in different galvanometers it was not considered practical to attempt measurements with a greater accuracy.

The mica condenser (free charge capacity) is by far the most convenient working standard for the comparison of electrical quantities. Its capacity should be tested from time to time on account of possible permanent changes. This is most conveniently accomplished by means of a standard mutual inductance coil whose coefficient is determined by comparison with the condenser when its capacity is first measured.

On closed circuit work, whenever it is practicable, the galvanometer circuit should be opened immediately after all the measureable part of the electrical discharge has passed through it. The quantities are then compared with the galvanometer on open circuit. When it is necessary to leave the galvanometer circuit closed during a throw the induced quantity can be compared with the known one from the condenser by discharging the condenser through the galvanometer and then immediately closing the circuit.

When during a comparison of the quantities the circuit is changed from a closed to an open one or the reverse, the thermo-electric currents of the circuit must first be eliminated or a correction made for their effect.

Observing the precautions and using the methods described in this paper, the moving-coil galvanometer can be employed with ease for measuring electrical quantities to the highest degree of accuracy attainable with direct deflection methods.

Physical Laboratory,
The University of Minnesota,
June 12, 1906.

# OPTICAL PROPERTIES OF CARBON FILMS.[1]

By Herbert A. Clark.

PURE carbon has been generally supposed to be a black body. Rosicky[2] in 1878, and later Stark,[3] investigated smoke films. The latter considered a smoke film as a turbid medium of air and carbon, and concluded that its dispersion is between that of air and of pure carbon. Ångström,[4] working in the infra red, obtained a rapidly increasing absorption in the case of lampblack from a wave length of 9,000 $\mu\mu$ down to 690 $\mu\mu$. Wood,[5] in 1901, using prismatic methods on smoke films, found the red rays retarded more than the blue, from 663 $\mu\mu$ to 414 $\mu\mu$; and, using interference methods, that films deposited on plate glass inside an electric lamp globe seem to show the same. For the latter films, he obtained a refractive index of 2.2 for the *D* line.

About the same time, E. L. Nichols[6] and Blaker[7] found that carbon rods and incandescent lamp filaments, both "treated" and "untreated," show, as their temperature increases, a more rapid increase in the radiation of the spectrum in the yellow than in the red or blue. Dr. Brace suggested[8] that the electro-magnetic theory shows that this increase in the radiation and the anomaly as found by Wood, both point to an absorption band in the yellow. Nichols[8] had found a maximum of absorption in the visible spectrum at the wave length 520 $\mu\mu$, in the case of lampblack. B. E. Moore and Ling[9] found the same in deposits on incandescent lamp globes at the wave length 635 $\mu\mu$, from "treated" filaments, but not from "untreated" filaments. Neither Rosicky[1] nor Stark[2] noticed this maximum in the absorption.

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[1] Read in part before the Am. Phys. Soc. at Chicago, April, 1905; and in part before the meeting at New York, December, 1905.

[2] Rosicky, Wiener Berichte, 78, II., p. 407, 1878.

[3] Stark, Wied. Ann., Vol. 62, p. 353, 1897.

[4] Ångström, Wied. Ann., Vol. 36, p. 715, 1889.

[5] Wood, Phil. Mag., VI., Vol. 1, p. 407, 1901.

[6] Nichols, Phys. Rev., Vol. 13, p. 129, 1901.

[7] Blaker, Phys. Rev., Vol. 13, p. 345, 1901.

[8] Nichols and Blaker, Phys. Rev., Vol. 13, p. 378, 1901.

[9] Nichols, Am. Jour. Sc., Vol. 34, p. 277.

Nichols,[3] working also with a prism of asphalt, which he considers a solution of carbon, determined the refractive index at four points in the red and yellow; and found an anomaly at a wave-length of 568.2 $\mu\mu$, with a refractive index of 1.6339. In the infra red, he found the absorption of asphalt to be very similar to Ångström's[4] values for lampblack, only that the change is much more abrupt.

None of these investigators, however, so far as I know, have determined by direct methods, the reflection, the refraction, and the absorption, all from the same specimen of pure carbon in a dense form. At Dr. Brace's suggestion, I have attempted to do this. This problem presupposes the use of transparent films of carbon. As yet, films of two kinds only have been considered; namely, those produced by Wright's[5] cathode method of deposit, and those obtained from the inside of incandescent lamp globes.

## Making the Films.

Longden[6] has shown that the character and the rate of deposit from a cathode upon a glass plate in a vacuum, depend upon the vacuum, the electromotive force, the current density over the cathode surface, and the distance from the cathode to the glass plate, as well as upon the material of the cathode. A vacuum tube (shown in cross section in Fig. 1) was so constructed that these conditions might be varied at will to produce the best results. It was made of two ordinary low form glass bell jars; the flanges of which were ground on a plane surface, so that they fit closely together, flange to flange. *C* is a carbon cathode, surrounded by mica. A hole in the upper mica sheet at *D* allows the cathode discharge to deposit carbon on the lower face of the glass plate, *A*. This plate is supported by the anode, *B*, a sheet of brass. The anode, in turn, is carried by a metallic stem, *M*, the lower end of which is of square cross section; the upper end is threaded. By turning the ground joint, *H*, the glass plate may be moved into the cathode stream, or out of it; by turning *K*, the distance between cathode and plate can be varied. The electric circuit in the tube is from the anode terminal, *F*, through a wire to a threaded nut in *K*; through the stem, *M*, to the anode, *B*; through the gas to the cathode, *C*; through a wire protected by a glass tube to a mercury cup, *E*; thence to the cathode terminal, *G*. Ordinary stop cock grease served to make the joints, all of which are ground glass, perfectly air tight. The cathode was made by combustion of granulated sugar, which is considered by chemists to yield the purest form of carbon, excepting the diamond.

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[1] Rosicky, l. c.

[2] Stark, l. c.

[3] Nichols, Phys. Rev., Vol. 14, p. 204, 1902.

[4] Ångström, l. c.

[5] Wright, Am. Jour. Sc., III., Vol. 13, p. 49, 1877.

[6] Longden, Phys. Rev., Vol. 11, p. 40, 1900.

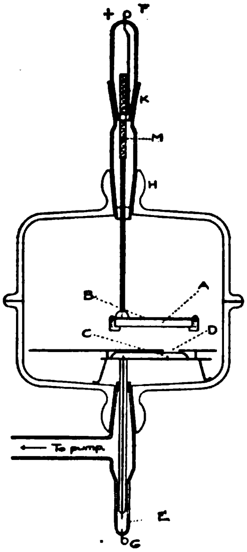

Fig. 1.

The films were deposited in atmospheric air which had been dried carefully, at low pressure, in contact with phosphorus pentoxide. A high potential storage battery served as a source of current, which was unidirectional. The best conditions for depositing carbon in air were found by trial to be as follows: a voltage of about 1,100; a current density of about .05 milliampere per square millimeter of cathode surface; a distance from cathode to glass plate of about fifteen millimeters; and such a gas pressure that the Crookes' dark space extended 5 or 6 millimeters from the cathode. The gas pressure was not measured definitely, but was less than one millimeter of mercury. Since slight changes in gas pressure change the resistance of the tube very appreciably, a galvanometer in series with the tube was used to determine the constancy of the gas pressure.

The films, under carefully adjusted conditions of deposit, were slightly prismatic, were reddish brown or black in color by transmitted light, appeared perfectly homogeneous and highly polished to the naked eye, varied in thickness from 0 to 10 $\mu$ and in transparency from 0 to 100 per cent., according to the thickness.

Viewed by reflected white light, they show beautiful interference bands, up to five or ten orders. They are almost as easily injured by rough usage as is a half-silvered coat on an interferometer plate, but seem to be independent of time changes except for a cracking and scaling off of the thicker portions. Those used were about one year old when measurements were made.

The second kind of films was unusually heavy deposits found on the inside walls of an ordinary incandescent lamp, which had been run at an abnormal voltage. The exact composition of the carbon filament in this case is not known.

## TEST FOR ANOMALOUS DISPERSION.

The supposed pressure of an anomaly in the refractive index curve of carbon led to making a test for this, by a method devised by Dr. Brace.[1] If light reflected from the two surfaces of a thin film is resolved by a prism or a grating, the spectrum will be crossed by dark lines, or "spectral bands," at those wave-lengths for which destructive interference occurs. If this film has an anomaly in its dispersion, the "spectral bands" will be variable in width; but they will coincide in width with similar bands from an air film at a maximum or a minimum point in the dispersion curve, if the order of interference is the same for the two films at this wave-length. Between the maximum and the minimum points, the "air bands" will be narrower than those of the medium; elsewhere the "air bands" will be the broader. Or, if the anomaly is very slight, the maximum and minimum may coincide, giving a point of inflection; in this case, the "air bands" will be broader on both sides of this point.

Two sets of "spectral bands" can be compared directly for this test, either with the eye or by photography, by means of a device shown in Fig. 2. A second collimator, *H*, is inserted into the side of the usual collimator, *C*, of an ordinary spectrometer. A mirror, *A*, set at an angle of 45° to either line of collimation, covers half the cross-section of *C*. The upper half of one collimator slit and the lower half of the other are covered with black paper. Then two spectra are seen in the eye-piece of the observing telescope;

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[1] Brace, PHYS. REV., Vol. 21, p. 291, 1905.

one in the upper half of the field, the other in the lower. By carefully adjusting *A*, these two spectra may be made to coincide throughout, line for line, the dividing line between the two becoming almost a vanishing line. *B* is a glass plate holding a thin film of the substance under investigation. A very small mirror, *D*, shown in the enlarged diagram, Fig. 3, enables light to be reflected at nearly normal incidence, from the film into the collimator. The use of this small mirror is far more satisfactory than that of a small, totally reflecting prism inside the collimator, one 45° edge of the prism serving as one edge of the slit; as the prism produces too much diffuse radiation inside the collimator, when highly absorbing substances are examined. Reflection from the two surfaces of the film gives "spectral bands," which may be compared with similar bands obtained from the surfaces of the air space between two glass plates, *E*. If this space is prismatic, "air bands" of any desired order, to coincide with the order of those from the film, may be brought into the telescope by sliding along the plates, *E*, in front of the slit. A Nernst lamp was used effectively as a source of light. Ten "spectral bands" between wave-lengths of 687 $\mu\mu$ and 472 $\mu\mu$ were obtained; but no anomaly was detected, although the irregularity in the dispersion curve (*A*, Fig. 9) suggests a very slight anomaly in the region of the *C* line.

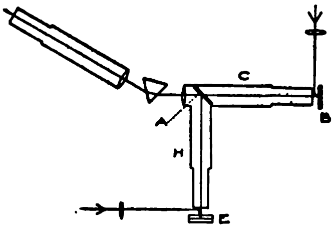

Fig. 2.

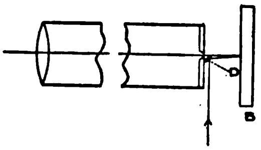

Fig. 3.

## THE INTERFEROMETER SYSTEM.

In determining the refractive index, interference methods were used entirely, in preference to prismatic. The interferometer employed was of the Jamin type, essentially the same as the one used by Cartmel.[1] Certain slight changes in arrangement and adjustment proved so advantageous, however, that a description is here given. In Fig. 4, *a* is the source of light, a Nernst glower; *b* is an adjustable slit in a screen; *c* is a nicol prism; *d* and *d'* are achromatic lenses of 25 cm. focal length; *e* and *e'* are the half silvered plates, and *f* and *f'*, the full silvered mirrors of the interterometer; *k* and *k'* are mica strips, the latter being a compensator; *n* is the film under investigation; *h* is a spectroscope; and *g* is a mirror, which allows the spectroscope to be placed in such a position that the operator can easily reach all parts of the system without changing his position.

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[1] Cartmel, Phil. Mag., VI., Vol. 6, p. 214, 1903.

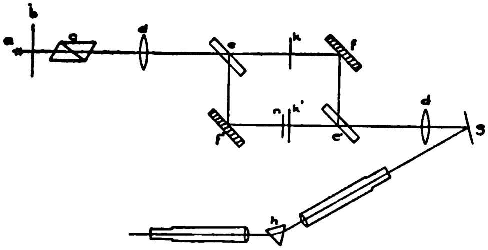

Fig. 4.

The interferometer plates are first adjusted for parallelism by alignment on an object at a distance of at least two miles, instead of only two or three hundred meters. It was found by trial that the consequent higher degree of accuracy in the parallelism of the plates made the "spectral bands" much more distinct and clear. The two light paths, *efe'* and *ef'e'*, are next made exactly equal by examining a very near object through them with the naked eye, and then the colored fringes of white light come into view. These fringes are then made vertical. No "spectral bands" will appear in the spectroscope as yet, for they are due to a slight difference in the two light paths. This difference is obtained by moving one of the mirrors *f* or *f'*, parallel to the direction of the ray from *e* to *f*. No further adjustment of the interferometer is needed to give clear, sharp "spectral bands," white light being used.

The nicol prism is turned so that its plane of polarization is vertical; consequently, nearly all of the light that is reflected from the half-silvered plates, comes from the rear (the half-silvered) surface. This makes the "spectral bands" more distinct, by eliminating all but one set of interfering rays. In case the lens, *d*, forms an image of the slit, *b*, upon the film, *n*; and the lens, *d'*, casts an image of that in turn upon the slit of the spectroscope, no "spectral bands" are seen. But let the spectroscope now be moved a few centimeters toward *g*, then bands are seen very plainly. In practice, however, the lens, *d*, is placed to form an image of the slit, *b*, upon the interferometer plate *e'*; then the lens, *d'*, produces an image of the film, *n*, upon the slit of the spectroscope. This allows a concentration of light upon the highly absorbing film under investigation at *n*, without recombination of the interfering rays into white light by the lens, *d'*.

Positions in the spectrum were determined by means of a tangent screw attached to the telescope, the micrometer head being about 6 cm. in diameter. This enabled the readings to be taken much more easily and quickly than if the usual circular scale had been used; and also made the order of accuracy of the readings somewhat higher, about the same as that of the settings. This method is much preferable to the use of a micrometer eyepiece, because of the unavoidable parallax while examining "spectral bands." The compensator *k'*, is the same kind as was used by Cartmel.[1] In addition, however, another piece of mica, *k*, of exactly the same thickness and with its optic axis in the same direction, is put in the other interferometer path. Another plate of glass of exactly the same thickness and composition as that of the one upon which the film, *n*, is deposited, is placed next to *k*. The two light paths, *efe'* and *ef'e'*, are thus identical except for the presence of the film itself and for the slight increase of length of one light path *in air* over that of the other. Any observed differential dispersion, then, is not affected by the presence of the compensator or of the glass.

## THE REFLECTION ATTACHMENT.

To measure the absolute reflection of any surface directly, it is essential that the path of the beam of light which is reflected and the path of another beam, which is used for comparison, shall be identical from the source to the eye, except that the first beam suffers reflection from the surface considered. It is also essential that the two beams shall be identical in intensity at the source; or else, that each can be compared directly with a third, the intensity of which varies exactly with that of the beam being examined. The first essential condition is realized by the use of a reflection attachment for the spectrophotometer, described below. In the second condition, two alternatives are offered. The first is difficult to attain. The second is readily realized by the use of the Brace spectrophotometer,[1] to one collimator of which the above attachment is fastened. The illumination of the two collimator slits comes from opposite sides of one point in an acetylene flame. Any gradual variations in the intensity of the source, then, can not affect the results, unless the intensity of the two sides of the flame at the same point should vary unequally; which is not likely. The adjustments of the spectrophotometer have been given by Tuckerman.[2]

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[1] Cartmel, l. c., p. 217.

The instrument readings taken, when the illumination for one collimator slit is reflected from the surface under consideration, are designated as the "reflection readings"; those taken when an identical beam does not suffer this reflection, the "direct readings." The absolute value of the reflection follows directly, then, as the ratio of the "reflection reading" to the "direct reading." The upper part of Fig. 5 shows a plan and the lower part, a side elevation, of the reflection attachment. *A* is the slit end of one collimator; *B* and *C* are small, totally reflecting prisms. *B* may be rotated by means of a crank, *D*, about an axis approximately parallel to the line of collimation, *HK*, through an angle of nearly 90°, fixed by adjustable stops (not shown in the figure). Prism *C* is arranged to slide from the position shown in the figure to a position directly over prism *B*, by means of the long guard arm *E*. Projections at either end of *E* are carefully fitted into slots in the bed plate, *F*. This allows the motion of *C* to be made parallel to the line of collimation. This motion is also regulated by adjustable stops (not shown). The operation is as follows. Light from the source behind strikes prism *B*, is reflected down to the horizontal plate, *M*, whose reflection is to be measured, then up to prism *C*, then into the slit of the collimator, *A*; and a "reflection reading" is taken. Prism *B* is next rotated (nearly 90°) until it reflects the light up; prism *C* is moved over it, reflecting the ray again into the slit; and a "direct reading" is taken. To make the light paths in the two collimators symmetrical, two prisms corresponding to *B* and *C*, cemented together with Canada balsam, were placed in front of the other collimator slit.

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[1] Brace, Phil. Mag., V., Vol. 48, p. 420, 1899; also Astrophys. Jour., Vol. 11, p. 6, 1900.

[2] Tuckerman, Astrophys. Jour., Vol. 16, p. 145, 1902.

The adjustment of the reflection attachment is as follows. An acetylene flame is put at the ocular slit of the spectrophotometer,

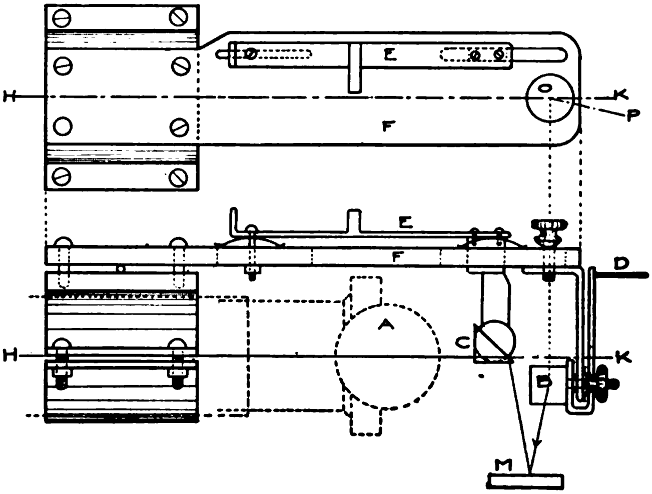

Fig. 5.

whence light passes through in a direction opposite to the usual one; hence the beams from the two collimators reach the plane in which is placed the source, ordinarily. Between each collimator slit and this plane is an achromatic condensing lens, forming an image of each slit upon the plane. By suitable adjustments, these images of the two slits are made to coincide, for both the "reflection" and the "direct reading" positions of the movable prisms. Further adjustments will make both the "reflection" and the "direct reading" beams pass through the same part of the condensing lens, as is determined by cross wires over the lens. If, now, prism *B* be tilted on its base through a definite angle, and its axis of rotation be moved about a vertical axis through a definite angle to a position, *OP*, light will pass through it perpendicular to both faces, and along identical paths, in its two positions; except that for one, the beam enters *B* where in the other it emerges, and *vice versa.*[1] Further, the objective of the telescope, which has a focal length of 300 mm., is diaphragmed down to 5 mm. in diameter, making an angular aperture of about 1°. The light paths for the two positions of prisms *B* and *C* are now identical from source to ocular slit, except for that part between them, where reflection takes place in one case. That this distance is greater for the "reflection readings" than for the "direct readings" is immaterial, if the intensity of the source over the area considered is uniform at any one instant. This area is about 1 sq. mm. for an angle of incidence of 5.75° upon the plate *M*, whose reflection is to be measured. At this angle, determined by a distance of 2 cm. between *B* and *M*, all of the readings were taken. The advantages of this method are: (1) the absolute reflection is measured directly for the chosen angle of incidence, as is shown above; (2) since the reflecting surface is horizontal, the method may be used for liquids; and (3) the area considered is small, — not greater than 0.4 mm. square in this case, — thus giving the value at a point, instead of an average value over a surface. The surface as a whole, therefore, need have no definite curvature, — it is necessary only that it be plane over a very small area.

## TRANSMISSION.

Measurements of the transmission of the films were made in the visible spectrum with the Brace spectrophotometer. Tables II. and III. give two sets of readings for the transmission of film No. 9, a cathodic film, at a point where its actual thickness is 4.67 $\mu$; Table I., of film No. 15, an incandescent lamp film, the thickness being .236 $\mu$. The "transmission" is given as the ratio of the intensity of light through the film, to that of light through the clear glass upon which the film is deposited, the two intensities being determined at places not more than 4 mm. apart. These results are shown graphically in Fig. 6; curve *A* is an average from the two sets of readings on film No. 9; curve *B*, for film No. 15. If there is a

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[1] It is thus necessary to select a prism whose faces are polished alike.

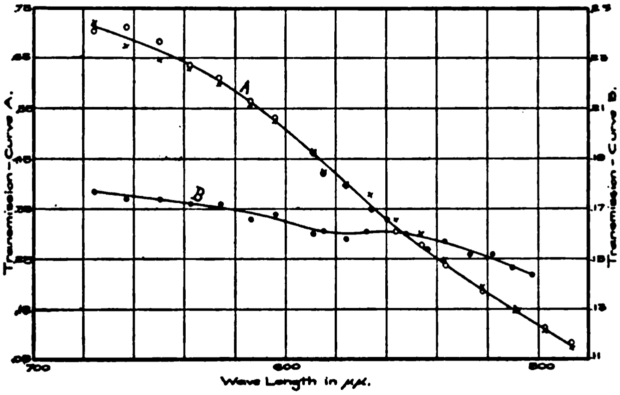

Fig. 6.

## Table I.

*Transmission of incandescent lamp film, No.* 15 ; *thickness,* 0.236 μ.

| Wave-length. | Transmission. | Wave-length. | Transmission. |
|---|---|---|---|
| — | — | 576 | .158 |
| 676 | .177 | 568 | .161 |
| 663 | .174 | 560 | .166 |
| 650 | .174 | 552 | .160 |
| 638 | .172 | 544 | .154 |
| 626 | .172 | 537 | .157 |
| 614 | .166 | 527 | .152 |
| 604 | .168 | 518 | .152 |
| 589 | .160 | 510 | .147 |
| 585 | .161 | 502 | .144 |

## Table II.

*Transmission of cathodic film, No.* 9; *thickness,* 4.67 μ.

| Wave-length. | Transmission. | Wave-length. | Transmission. |
|---|---|---|---|
| 676 | .720 | 566 | .380 |
| 663 | .675 | 556 | .330 |
| 650 | .646 | 546 | .304 |
| 638 | .630 | 537 | .250 |
| 626 | .596 | 522 | .199 |
| 614 | .560 | 508 | .148 |
| 604 | .526 | 497 | .106 |
| 589 | .465 | 486 | .074 |
| 585 | .425 | 477 | .054 |
| 576 | .401 | | |

TABLE III.

*Transmission of cathodic film, No.* 9 ; *thickness*, 4.67 $\mu$.

| Wave-length. | Transmission. | Wave-length. | Transmission. |
|---|---|---|---|
| 676 | .702 | 566 | .350 |
| 663 | .711 | 556 | .305 |
| 650 | .681 | 546 | .277 |
| 638 | .635 | 537 | .237 |
| 626 | .611 | 522 | .187 |
| 614 | .563 | 508 | .147 |
| 604 | .531 | 497 | .114 |
| 589 | .461 | 486 | .083 |
| 585 | .422 | 477 | .055 |
| 576 | .397 | | |

maximum in the absorption, such as was found by Nichols[1] for lampblack or by Moore and Ling[2] in the case of incandescent lamp deposits, it is very slight.

The transmission in the ultra-violet was obtained in a qualitative way by means of a Schumann quartz spectrograph. An induction coil arc between terminals of an alloy of cadmium, zinc and aluminium was the source of light. The well-known method of "crossed prisms" was used. Very thin cathodic films on quartz plates were placed before the slit, with the refracting edge of the slightly prismatic film perpendicular to the slit. Under these conditions, photographs were taken with varying times of exposure. If the film over one end of the slit is thin enough to transmit light of a certain wave-length, but thick enough at the other end to be opaque for the same wave-length, the effect upon the photographic plate will be an apparent shortening of the slit. Fig. 7, showing three exposures on one plate, brings out this effect plainly. The faint exposure was a short one, taken before the film was put in place, to locate points in the spectrum. The other two exposures, as well as every other one taken with the film before the slit, show an exposure over the

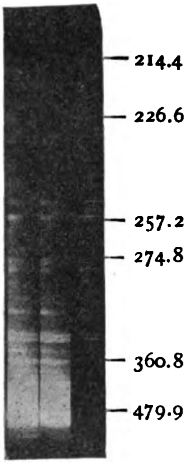

Fig. 7.

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[1] Nichols and Blaker, l. c.

[2] Nichols, Am. Jour. Sc., Vol. 34, p. 277.

whole length of the slit at the red end at a uniform decrease in length for shorter wave-lengths as far as 226.6 $\mu\mu$; beyond this, the absorption is apparently complete as far out as 189.6 $\mu\mu$, the last wave-length detected when the slit is not covered by a film. A true absorption band, if present, would have shown first a decrease in length, then an increase.

### Reflection.

The reflection was measured as previously described. No attempt was made to polish any film, — a camel's hair brush will scratch the hardest cathodic carbon surface. In every case, the best reflecting portion of the surface was selected for measurements, which were made on the air surface. These were probably affected very slightly by reflection from the clear glass surface on the back side of the glass plate upon which the film was deposited. A pronounced and puzzling waviness in the reflection curves as first obtained, which varied from point to point on the reflecting surface, was found to be due to interference between the two surfaces of the film. When the reflecting surface of the film is examined with the spectrophotometer without an eyepiece and with the ocular and the collimator slits both very narrow, characteristic interference bands are plainly seen. These bands move across the field of view, when the film is shifted in its own plane toward either a thicker or thinner part. The effect of this interference is eliminated as follows. The telescope objective is diaphragmed by a vertical slit 1.5 mm. wide, approximately wide enough to show one light interference band or one dark band at a time, at the ocular slit. Then the reflection is measured for one wave-length, at one point on the film. The film is next moved in its own plane a very small distance, as described above, and the reflection again determined. This process is repeated until the maximum and the minimum in the reflection can be determined for any one wave-length. The whole procedure is then repeated for other wave-lengths. The average of these values is given in the results as the true reflection. The films are sufficiently prismatic to change the order of interference by one, for a motion as described above, of .35 mm., determined by calculation from the known variation in thickness of the film, and also by trial. Within this limit, the true reflection is considered a constant, although it varies considerably in going a distance of 10 mm.

The data obtained from film No. 9 are given in Table IV. and represented graphically in Fig. 8. Aschkinass[1] gives the reflection of polished gas carbon as 4.4 per cent. at the $D$ line, increasing to nearly 100 per cent. for Hertzian waves. The reflection of a cathodic carbon surface, at the $D$ line, is seen from the curve to be 4 per cent. There is apparently a very slight rise in the reflection curve of cathodic films at 630 $\mu\mu$, corresponding closely to the slight anomaly as shown in curve $A$, Fig. 9. If there is a corresponding variation in the transmission, it is very slight. Nichols and Blaker[2] found a maximum in the rate of increase of radiation

### TABLE IV.

*Reflection of cathodic film, No. 9.*

| Wave-length. | Maximum Reflection. | Minimum Reflection. | True Reflection. |
|---|---|---|---|
| 673 | .0695 | .0530 | .0613 |
| 650 | .0530 | .0377 | .0454 |
| 626 | .0604 | .0424 | .0514 |
| 599 | .0477 | .0361 | .0419 |
| 576 | .0395 | .0354 | .0375 |
| 556 | .0351 | .0309 | .0330 |
| 537 | .0367 | .0314 | .0341 |
| 518 | .0380 | .0334 | .0357 |
| 502 | .0370 | .0346 | .0358 |
| 490 | .0333 | .0299 | .0316 |

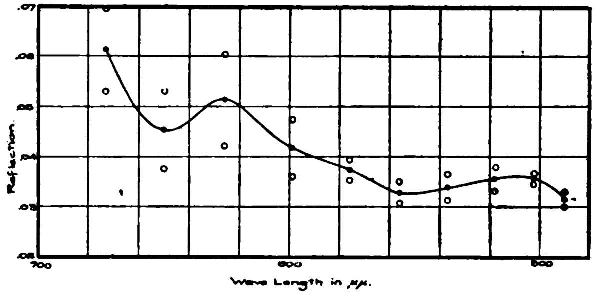

Fig. 8.

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[1] Aschkinass, Ann. d. Physik, IV., Vol. 18, p. 373, 1905.

[2] Nichols, PHYS. REV., Vol. 13, p. 129, 1901; and Blaker, l. c.

with temperature, using carbon rods and filaments, between the wave-lengths 620 $\mu\mu$ and 700 $\mu\mu$, the exact position varying with the temperature. The reflection of the incandescent lamp films was not obtained, because of their curvature. The refractive index curve for these films, as well as the anomaly found by Wood[1] in similar films deposited on plate glass inside an incandescent lamp globe, suggests the probability of an abrupt change in their reflection.

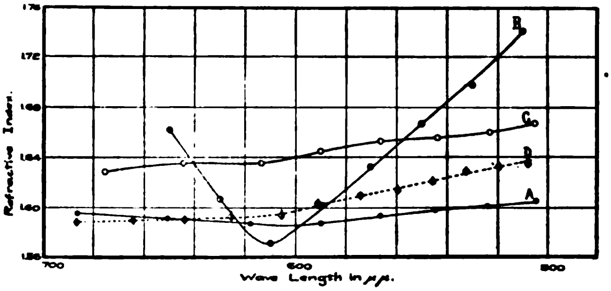

Fig. 9.

## Refractive Index of Cathodic Films.

To obtain the refractive index of a film by interference methods, it is simply necessary to determine the "air thickness" and the "optical thickness" at the same point, in terms of the wave-length considered. The ratio of the latter to the former gives the index.

*To determine the air thickness*, the carbon film is cleaned away from a portion of the glass plate and another plate is put over it, forming a layer of air between the plates on one hand and the front plate and the film on the other. Then if light reflected from these surfaces is resolved by a prism or a grating, two sets of "spectral air bands" will be seen, as when the spectrometer with two collimators is used: one, due to interference between the two inner glass surfaces; the other, to interference between the free carbon surface and the glass surface over it. If these surfaces are slightly inclined to each other, in such a way that the "spectral bands" are parallel to the collimator slit, and are approximately plane, the "air thickness" of the carbon film at any point is readily found by a formula due to Dr. Brace;[1] or, by a slightly simpler formula, as follows. Let $n_1$ be the number of "spectral bands" between two definite points in the spectrum, arising from interference between the glass surfaces; let $n_2$ be the corresponding number, after the reflecting plates have been moved a certain distance in their own plane; while $m$ represents the number of "spectral bands" that have moved past any wave-length, $\lambda$, during this shift. Further, let $N_1$ be the "order of interference" — twice the distance between the two reflecting surfaces at the initial position — measured in terms of $\lambda$. Then

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[1] Wood, l. c.

$$N_1 = \frac{n_1 m}{n_2 - n_1}.$$

$m$ is $+$ or $-$, according as the shift of "spectral bands" is toward the red or toward the blue. Let $N_2$ be the corresponding "order of interference" between the glass and the carbon surfaces at the same point. Then $N$, the "air thickness," follows directly:

$$N = \frac{N_1 - N_2}{2}.$$

The cathodic films are highly transparent to the longer wave-lengths; hence, the assumption was made that there is the same change of phase on reflection from carbon as from glass, for these wave-lengths. (There is no evidence of a sudden change of phase, such as Cartmel[2] noticed in the case of fuchsin.) This assumption is the same as was made by Pflüger[3] in the case of reflection of red light from fuchsin, which is many times more opaque than carbon, even for those wave-lengths for which the former is most transparent. Since this assumption requires the choice of dark bands[4] for measurements, these were made in every case by setting upon the dark, rather than upon the light, bands.

*To obtain the "optical thickness,"* two methods were used. The first, or "spectrometer method," is identical in principle with the method just described above, for the "air thickness." The upper glass plate is removed, and interference takes place between the two surfaces of the film, giving "carbon bands" in the spectrum, from which $M$, the "optical thickness," is obtained. The refractive index, $\mu$, for the wave-length $\lambda$, is the ratio of $M$ to $N$, as above. If $\lambda_1$, $\lambda_2$, $\cdots$, $\lambda_k$ are the wave-lengths, from $\lambda$ toward the blue, corresponding to the centers of the successive "carbon bands," the refractive index for each of these wave-lengths is

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[1] Brace, Phil. Mag., V., Vol. 48, p. 350, 1899; also Rendtorff, Phil. Mag., VI., Vol. 1, p. 359, 1901; and Williams, PHYS. REV., Vol. 18, p. 280, 1904.

[2] Cartmel, l. c., p. 222.

[3] Pflüger, Wied. Ann., Vol. 65, p. 203, 1898.

[4] Brace, PHYS. REV., Vol. 21, p. 291, 1901.

$$\mu_k = \frac{(M+k)\lambda_k}{M\lambda}\mu ,$$

where $M$ is the "optical thickness," in terms of $\lambda$. Table V. gives the refractive index obtained by this method, for cathodic film No. 7, which gave an especially distinct set of "spectral bands." These results are represented by curve $A$, Fig. 9. Film No. 9 gave a similar curve, though about 3 per cent. higher in the red, rising to 4 per cent. in the blue. (See Table VI., and curve $C$, Fig. 9.) Film No. 9 was more highly absorbing than No. 7 for the same thickness; hence was probably denser.

### Table V.

*Refractive Index of cathodic film, No. 7; spectrometer method.*

| Order, $M$. | Wave-length. | Refractive Index. | Order, $M$. | Wave-length. | Refractive Index. |
|---|---|---|---|---|---|
| 19 | 687 | 1.596 | 24 | 545 | 1.599 |
| 20 | 651 | 1.592 | 25 | 524 | 1.601 |
| 21 | 618 | 1.588 | 26 | 505 | 1.605 |
| 22 | 590 | 1.588 | 27 | 487 | 1.609 |
| 23 | 567 | 1.594 | 28 | 472 | 1.617 |

### Table VI.

*Refractive index of cathodic film, No 9; spectrometer method.*

| Order, $M$. | Wave-length. | Refractive Index. | Order, $M$. | Wave-length. | Refractive Index. |
|---|---|---|---|---|---|
| 19 | 676 | 1.629 | 23 | 566 | 1.653 |
| 20 | 646 | 1.636 | 24 | 544 | 1.656 |
| 21 | 614 | 1.636 | 25 | 523 | 1.660 |
| 22 | 589 | 1.645 | 26 | 505 | 1.667 |

This method is very advantageous, where the films are prismatic and are neither too thick nor too thin to give good bands; because the retardation of one interfering ray over the other takes place entirely in one medium.

The second, or "interferometer method," of obtaining the "optical thickness," in which the interferometer previously described was used, can be used with much thicker films than can the "spectrometer method"; for light traverses the film, which is strongly absorbing, only once in this type of interferometer. It can also be used for much thinner films—films too thin to give "spectral bands"—; for "spectral bands" may be introduced by adjusting the interferometer. As previously described, the instrument is first so adjusted that the retardation in one interferometer path over that in the other is due to carbon, or to air, or to both, and to nothing else. The carbon film, *n*, Fig. 4, is traversed by the lower half of the beam of light in one path; the rotating part of the mica compensator, *k'*, is in the upper part of the same beam. Two sets of spectral bands appear in the spectroscope, *h*, one above the other; as when the spectrometer with two collimators is used. The retardation due to the carbon, in terms of the number of "spectral bands" shifted past any one wave-length, $\lambda$, is measured roughly by slowly pushing along the glass plate carrying the carbon film, from a point where the retardation due to the carbon is zero. The compensator is then turned until the retardation due to the mica is the same at $\lambda$, at the center of a dark band, as that due to the carbon. The process is repeated for other wave-lengths.

The refractive index for any wave-length is

$$\mu = \frac{N + r}{N},$$

where $N$ is the "air thickness" and $r$, the retardation, both measured in terms of $\lambda$. The refractive index of the cathodic films as determined by this method, agrees well with that found by the other method, except in the green and the blue, where the absorption is so great that the spectrometer method is not very accurate. Table VII. and curve *D*, Fig. 9, show the index of film No. 7, obtained by this method. (Compare Table V. and curve *A*.) When the inter-

### Table VII.

*Refractive index of cathodic film, No. 7; interferometer method.*

| Wave-length. | Retardation, $r$. | Refractive Index. | Wave-length. | Retardation, $r$. | Refractive Index. |
|---|---|---|---|---|---|
| 687 | 3.49 | 1.589 | 576 | 4.32 | 1.610 |
| 665 | 3.61 | 1.590 | 560 | 4.46 | 1.614 |
| 645 | 3.73 | 1.591 | 546 | 4.63 | 1.621 |
| 626 | 3.86 | 1.594 | 533 | 4.80 | 1.629 |
| 605 | 4.00 | 1.595 | 520 | 4.95 | 1.633 |
| 591 | 4.15 | 1.603 | 508 | 5.09 | 1.635 |

ferometer is used, the method of mixed bands[1] should be applied. However, with the order of thickness used in this work, the error due to neglecting this correction is very small, since the mixed bands include air and carbon bands only.

## Refractive Index of Incandescent Lamp Films.

The incandescent lamp films were but very slightly, if at all, prismatic and were on curved surfaces; consequently, the methods of measurement used in determining the refractive index of cathodic films, need some modifications. Obviously, the spectrometer method could not be used; hence, the interferometer method was employed. A lamp was broken into bits, and a piece selected that gave approximately straight "spectral bands" when placed in the interferometer, the light being resolved by a spectrometer with a very short, narrow narrow slit. The incandescent lamp films not being sufficiently prismatic, the order of retardation could not be obtained roughly, as it was for the cathodic films. Instead, the interferometer is set for the central white band in one half of the field, as seen in the spectrometer; then, one of the interferometer plates is moved until the same condition is obtained in the other half of the field, and the consequent shift of bands past any wave-length is counted. This shift, for lamp films, was always less than one band. The exact retardation was determined from the mica-compensator readings as follows. The compensator was carefully calibrated throughout the spectrum, for a shift of each whole band from 1 to 5. The retardation caused by rotating the compensator is

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[1] Brace, Phys. Rev., Vol. 21, p. 294, 1905.

$$r = \frac{t(\mu - 1)}{\lambda}\left(\frac{1}{\cos\theta} - 1\right),$$

where $t$ is the "air thickness" of the mica; $\theta$, the angle through which the compensator is turned for the wave-length, $\lambda$; and $\mu$, the refractive index of the mica in the direction of the ray. $\mu$ is constant for values of $\theta$ from 0° to 20°, corresponding to values of $r$ from 0 to 5, as can be shown by plotting values of $r$ and $(1/\cos\theta - 1)$. This makes

$$r = K\left(\frac{1}{\cos\theta} - 1\right),$$

in which $K$ is calculated from the observed values of $r$ and $\theta$ within the limits just given. From this equation, calibration curves were calculated and plotted for values of $r = 0, 0.05, 0.1, 0.2, \cdots, 1.0$, since $r$ was always less than unity in practice. The actual retardation caused by the lamp films was then obtained by interpolation from these curves.

To determine the "air thickness" of lamp films, Newton's rings were used. Upon the film side of the bit of glass selected above — from a part of which the film had been cleaned away — was placed another selected piece of the same globe, carefully cleaned all over, and the whole illuminated with strong sodium light. This arrangement gave two sets of Newton's rings, shifted past one another slightly, just as were the "spectral bands" above. This shift was measured for light at nearly perpendicular incidence, by means of a low-power micrometer microscope; and from it, the "air thickness" of the film was calculated. There was a little uncertainty at first, whether the shift of the sodium bands was a part of a band only, or a certain number plus that part of a band. This is settled definitely, however, by the fact that, if the shift is assumed to be a part only of a band, the index becomes 1.602; while, if the shift is assumed to be one whole band plus that fraction, the resulting index is only 1.3, — an improbable value. The "air thickness" of incandescent lamp film No. 15 is thus determined to be .402 wave-length, at the $D$ line. $\mu_D$ is then determined from the equation given above,

$$\mu = \frac{N + r}{N}.$$

The refractive index for other wave-lengths is obtained from the equation,

$$\mu_x = 1 + \frac{r_x \lambda_x}{N_D \lambda_D}.$$

The results from the above film No. 15, are shown in Table VIII. and are represented by curve $B$ of Fig. 9.

TABLE VIII.

*Refractive index of incandescent lamp film, No. 15; interferometer method.*

| Wave-length. | Retardation, $r$. | Refractive Index. | Wave-length. | Retardation, $r$. | Refractive Index. |
|---|---|---|---|---|---|
| 650 | .241 | 1.662 | 570 | .263 | 1.633 |
| 630 | .228 | 1.607 | 550 | .287 | 1.667 |
| 610 | .222 | 1.572 | 530 | .312 | 1.698 |
| 589 | .242 | 1.602 | 510 | .344 | 1.741 |

The refractive index of every film examined shows anomalous dispersion, although it is very slight in all of the cathodic films. In these, the anomaly probably corresponds to a "point of inflection"[1] in the refractive index curve. There is a corresponding variation in the reflection of cathodic films, but little or no evidence of a variation in the absorption, even in the case of incandescent lamp films, in which the anomaly is most prominent. The lamp films examined were somewhat thicker and more porous than is usual with such films. Wood's films[2] were deposited on plate glass inside a lamp globe; hence the deposit was formed at a place much nearer the incandescent filament than in the case of mine. His were, in consequence, probably much denser than mine. This would account for his higher value of the refractive index, 2.2 for the $D$ line, as compared with my value of 1.6.[3] Amorphous carbon absorbs nitrogen so strongly that it probably is really a solution of nitrogen and carbon, as Stark[4] suggests for smoke films.

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[1] Brace, PHYS. REV., Vol. 21, p. 293, 1905.

[2] Wood, l. c.

[3] Professor F. Braun, of Strassburg, has kindly sent me a number of carbon films made by "flashing" a filament near a glass surface. He has shown (Ann. d. Physik, IV., Vol. 17, p. 359) that these films are deposited directly from the vaporous condition. Consequently, they are much denser than those I have thus far examined. I hope to be able to determine the optical properties of these later.

[4] Stark, l. c.

Its properties, therefore, are those of a solution, and not of pure carbon.

Different samples examined thus far vary so much, that it appears conclusive that the optical properties of carbon films, and probably of other substances as well, are not constant; but are complex functions of the conditions and methods of deposit. This is to be expected from the work of Kundt,[1] Hagen and Rubens,[2] Stone,[3] Longden,[4] Patterson,[5] Beilby,[6] and others, upon both the optical and the electrical properties of thin films of metals. The suggestion of Kundt and of Hagen and Rubens, that this variation for certain metals may be due to the formation of oxides, is not so satisfactory in the case of carbon, since its oxides are gases.

## RECAPITULATION.

1. The reflection, the absorption, and the refractive index of carbon films vary with the conditions and method of deposit.

2. There is a slight anomaly in the refractive index of cathodic carbon films, and a more pronounced one in the case of incandescent lamp films, at the wave-length $\lambda = 610\ \mu\mu$. The reflection curves of the former show a corresponding variation. Scarcely any variation, however, has been detected in the transmission curves of either class of films.

3. The transmission of cathodic films decreases almost uniformly from the red of the visible spectrum to the wave-length $\lambda = 226.6\ \mu\mu$, beyond which the films are completely opaque. Thus there is no pronounced absorption band.

4. The reflection of cathodic films *decreases* from a maximum in the red to a minimum in the blue of the visible spectrum. A slight rise, however, occurs at the wave-length $\lambda = 630\ \mu\mu$.

In conclusion, I wish to express my grateful appreciation of the assistance and inspiration given me in this work by the late Dr. D. B. Brace, and also of the excellent laboratory facilities placed at my disposal in the University of Nebraska, where it was done.

SYRACUSE UNIVERSITY, June, 1906.

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[1] Kundt, Phil. Mag. V., Vol. 26, p. 1, 1888.

[2] Hagen and Rubens, Phil. Mag., VI., Vol. 7, p. 164, 1904.

[3] Stone, PHYS. REV., Vol. 6, p. 1, 1898.

[4] Longden, l. c.

[5] Patterson, Phil. Mag., VI., Vol. 4, p. 652, 1902.

[6] Beilby, Proc. Roy. Soc., Vol. 72, p. 226, 1903.

# THE MOISTURE PRECIPITATED IN THE FOG CHAMBER PER CUBIC CENTIMETER.

By Carl Barus.

1. Elsewhere[1] I have shown that the combination of fog chamber with a large vacuum chamber and a sufficiently wide passageway, though affording superior practical advantages, and little if any inferiority in efficiency to the piston apparatus within the range of measurable coronas, nevertheless does not show the volume expansion of the air within the fog chamber either under adiabatic or under isothermal conditions. It makes no difference how rapidly the stop cock is manually closed, the conditions of the vacuum chamber are always impressed upon the fog chamber. The adiabatic and isothermal data may, however, be computed, if the volume ratio of the fog and vacuum chambers and the pressures before exhaustion (when the chambers are isothermally separated) and after exhaustion (when the chambers are isothermally in communication) are known; and these computations are simple because the reductions are practically linear.

When the vacuum chamber is large, moreover its pressures vary but slightly, and therefore the pressure observed at the vacuum chamber after exhaustion, when the two chambers are in communication, is very nearly the adiabatic pressure of the fog chamber. This result makes it easy to compute the water precipitated per cubic centimeter, without stopping to compute the other pressures, with a degree of accuracy more than sufficient when the other measurements depend on the size of coronas.

2. To show this, let $d$, $L$, and $\pi$ refer to the density, latent heat of evaporization and pressure of water (or other) vapor; let $\rho$, $k$, $c$, $t$, denote the density, specific heat at constant pressure, specific heat at constant volume and absolute temperature of the air, the water vapor contained being disregarded apart from the occurrence of condensation. Let the variables, if primed, belong to the vacuum

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[1] American Journal of Science.

chamber otherwise to the fog chamber. When used without subscripts, let them refer to isothermal conditions or to room temperature. Let the subscript 1 refer to the adiabatic conditions on exhaustion; the subscript 2 to isothermal conditions, if the chambers could be isolated immediately after exhaustion and allowed to heat and cool from the adiabatic state independently. This case is actually realized in the piston apparatus. Let the subscript 3, finally, refer to the isothermal conditions which prevail if the chambers are put in communication at a room temperature after exhaustion. Then the usual equations for the heat evolved in the condensation of vapor, leads easily to

$$\bar{d} = [d_1] - \rho_2 c(\bar{t} - t_1)/L \qquad (1)$$

where $\bar{d}$ is the density of saturated vapor at $\bar{t}$, if $\bar{t}$ is the temperature to which the wet air is heated from its adiabatic temperature $t_1$, in consequence of the condensation of water vapor, and where $[d_1]$ is the density of water vapor if cooled as a gas (*i. e.*, without condensation) from $t$ to $t_1$. Moreover,

$$[d_1] - \bar{d} = m, \qquad (2)$$

the mass of water precipitated per cubic centimeter by condensation, or the quantity sought.

If Boyle's law is assumed to hold both for the gaseous water vapor, $[d_1]$, and for the wet air, it is convenient to reduce equation (1) to room temperature (isothermal state), and it becomes

$$\bar{d} = d\frac{p_2 - \pi}{p - \pi} - \frac{\rho c}{L}\frac{p_2 - \pi}{p - \pi}\left(\bar{t} - t_1\right). \qquad (3)$$

If the vapor density of saturated water vapor is known at a temperature as low as $\bar{t}$,

$$\bar{d} = f(\bar{t}) \qquad (4)$$

so that $\bar{t}$ (the only unknown quantity in equation (3), since the equation of adiabatic expansion determines $t_1$) is found from the intersection of the curves (3) and (4). This is the method of Wilson[1] and of Thomson.

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[1] C. T. R. Wilson, Phil. Trans., London, Vol. 189, p. 298, 1897.

3. In the piston apparatus $p_2$ as well as $p$ may be read off at the gauges: but as stated above, this is not true when the fog chamber communicates directly with the vacuum chamber. In this case, however, $p_1$ is nearly given by $p_3$. Consequently it is expedient to reduce equation (1) to the adiabatic conditions, whence

$$\bar{d} = d \left(\frac{p_1 - \pi_1}{p - \pi}\right)^{c/k} - \frac{\rho c}{L} \left(\frac{p_1 - \pi_1}{p - \pi}\right)^{c/k} (\bar{t} - t_1) \qquad (5)$$

$$\tau_1 = \tau \left(\frac{p_1 - \pi_1}{p - \pi}\right)^{(k-c)/k} \qquad (6)$$

$$m = \frac{\rho c}{L} \left(\frac{p_1 - \pi_1}{p - \pi}\right)^{c/k} (\bar{t} - t_1) \qquad (7)$$

Here $\pi_1$, the vapor pressure at $t_1$, is usually negligible (about .5 cm.) as compared with $p_1$, and $p_1$ may in practice (where great accuracy is not demanded) be replaced by $p_3$, which like $p$ is read off, while $\pi$ holds at $t$, which is also read off.

4. In conclusion I will give a numerical example taken from a preceding paper, (l. c.) where

| Observed. | Computed. |
|---|---|
| $p = 76$ cm. | $p_1 = 46.1$ cm. |
| $\pi = 1.7$ cm. | $p_2 = 54\ 7$ cm. |
| $\rho = .00118$. | $t_1 = -17.8°$ C. |
| $p^1 = 43.5$ cm. | $\bar{t} = +5.25°$ C. |
| $p_3 = 45.5$ cm. | $t_1' = 24.1°$ C. |

If equation (3) is taken,

$$m = 5.36 \times 10^{-6} \text{ grams per cm.}^3$$

If equation (5) is taken,

$$m = 5.35 \times 10^{-6}.$$

If equation (5) is taken and $p_1$ replaced by $p_3$,

$$m = 5.30 \times 10^{-6},$$

the error being 1 per cent. of the true value, which is quite near enough in practice and admits of easy correction.

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# ON INCREASING THE CONSTANCY OF BATTERIES GIVING CURRENTS.

By W. P. White.

If a storage battery while charging is also made to give a current nearly equal to the charging current, very little electricity will flow through the battery, whose action is then to steady the voltage of the current source. The idea is familiar of using an accumulator battery in this way where storage of energy is a secondary consideration. An application of the same principle renders it possible, with an arrangement of primary or secondary batteries alone, to obtain current at a steadier voltage than would be possible with the same number of cells connected parallel. The arrangement is simple enough in theory: it may, however, deserve a brief description.

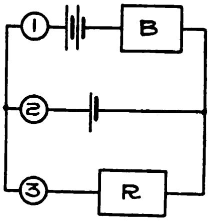

Fig. 1

The disposition of the cells is shown in the figure. Branch (1) contains a battery and a resistance box. The voltage in this branch is $V$ and the resistance $B$. Branch (2) contains another battery of smaller voltage, $v$, and of resistance, $b$. Branch (3) contains the apparatus through which it is desired to send constant current or current at constant voltage. Its resistance is $R$. By proper adjustment of the resistance, $B$, it is possible to make the current through branch (2) as small as we please, and therefore to keep the battery in that branch constant. At the same time the value of the current through (3) can be made to depend largely or entirely upon the constant battery (2), and only slightly, or not at all, upon the battery in (1), which sends the current. The current through (2), $I_2$, is,

$$\frac{VR - v(B + R)}{BR + b(B + R)}. \qquad \text{(I.)}$$

The condition for this to be zero is evidently

$$\frac{V}{v} = \frac{B + \mathrm{R}}{R}. \qquad \text{(II.)}$$

If $V = 2 \times v$, $B = R$. In this case, adjustment is particularly easy since any change in $R$ can be approximately compensated by making the same change in $B$. Moreover, this arrangement can be secured with the smallest possible number of cells, three. In what follows, it will be sufficient to discuss this particular case. If $V$ varies — as it must be supposed to do, otherwise there would be no object in using more than one cell — or if the adjustment of $B$ is not exact, the effect on the voltage of the battery in (2) will be small. For instance, if the current $I_1$ flowing through (1) causes a variation of 1 per cent. in $V$, the resulting current in (2) will be 2 per cent. of $I_1$, and should cause a variation in $v$ of less than .02 per cent.— usually much less. If the variation in $V$ is 10 per cent., the variation in $v$ may be as much as 2 per cent., in which case this arrangement is little better than the three cells in parallel.

The current which it is desired to regulate, $I_3$, equals

$$\frac{v + V\frac{b}{B}}{R + (R + B)\frac{b}{B}}. \qquad \text{(III.)}$$

This equals $v/R$ as long as the condition (II.) holds, regardless of the resistance in (2) or of any variation of $V$.

Hence by putting an ammeter in the branch (2) and adjusting $B$ so that $I_2$ remains approximately zero, $I_3$ can be kept as close to $v/R$ as desired — a somewhat troublesome arrangement, but one which might prove of value if it were necessary to get constant results with rather poor batteries. If $V$ or the adjustment of $B$ varies, $I_3$ will vary; that is, the conditions which cause a currrent through branch (2), and thereby may cause a variation in $v$ will also for another reason cause a variation in $I_3$, whether $v$ varies or not. This second variation is nearly proportional to $b/B$ and may be made very small. The arrangement of cells here described, therefore, works best with batteries of low resistance. It is also better adapted for increasing greatly the constancy of a battery already fairly constant than for improving a poor one. It is especially effective with storage cells, to which the writer has applied it. In particular, it is well suited to give constancy in the main current of potentiometers of very low resistance where storage cells of the usual capacity generally show troublesome fluctuations.

Geophysical Laboratory,
Carnegie Institution of Washington,
July 2, 1906.

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# THE CONSTANCY OF THERMOELEMENTS.

BY WALTER P. WHITE.

ELECTRICAL thermometers are coming more and more into use, not only for the measurement of extreme temperatures and other special work, but even to secure for calorimetry an instrument superior to the mercury thermometer. Among electrical thermometers the resistance thermometer, for temperatures below 1000°, has been the one mainly used where accuracy and great sensitiveness were especially desired. The possibilities of the thermoelement in these directions have therefore remained comparatively undeveloped, while the great advantages which it frequently offers for particular kinds of work have been attainable only by the sacrifice of exactness. Palmer,[1] however, has already shown that the thermoelement may become an instrument of precision comparable with the best thermometers of other types; and the attainment of similar results in other cases is a matter of no great difficulty.

The errors of the thermoelement are almost entirely due to a single cause, inhomogeneity, which renders parasitic electromotive forces liable to occur at any point along the wires, and makes the reading of the element subject to change with every temperature fluctuation throughout its length. Where the trouble is due to a change in the material of the wires, it can generally be prevented by care in using the element. The inhomogeneity of the original materials can usually be diminished by making a proper selection of wires, or corrected by suitable treatment afterwards, and the detrimental effect of what remains can always be reduced by various devices.

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[1] A DeForest Palmer, PHYS. REV., 21, p. 65, 1905.

The effect of inhomogeneities can easily be expressed by an extension of the ordinary formula, which gives the electromotive force of homogeneous thermoelements. In any metallic circuit, let $J$ be the junction between $E$ and $F$, two portions of wire, each homogeneous in itself but differing from the other in thermoelectric power by an amount, $\triangle H$. Suppose the middle points of $E$ and $F$ cooled to the same temperature, $\theta_0$, which may be as low as convenient. This cooling will not affect the thermoelectromotive force in the circuit, since it occurs within homogeneous portions of wire. If the temperature of $J$ is $\theta_J$ there will be a thermoelectromotive force between $E$ and $F$ equal to $(\theta_J - \theta_0)\triangle H$.[1] A similar expression obtains for every other point in the circuit at which there is a change in $H$. The total electromotive force therefore equals

$$\Sigma(\theta_J - \theta_0)\triangle H. \tag{1}$$

Since the temperature $\theta_0$ may be anything we please, it can be taken equal to 0, and equation (1) becomes

$$E = \Sigma\theta_J\triangle H. \tag{2}$$

In general, the variation in thermoelectromotive power along the circuit will be continuous. $E$ and $F$ may then be taken to be infinitesimal; the portion cooled to the temperature $\theta$ may be a second order infinitesimal (since the length of the cooled portion does not affect the thermoelectromotive force), and (2) becomes

$$E = \int \theta dH, \tag{3}$$

where the integration is to be carried over the whole circuit. $dH$ of course is itself a function of $\theta$.

The magnitude of the error due to inhomogeneity in any given case can easily be computed in accordance with formula (3) by a graphical method. This is illustrated in the following discussion of a contaminated platinum thermoelement in an electric furnace. The upper curve ($LMN$) gives the observed temperature gradient;[1] the next ($PQR$), the approximate thermoelectric power along the platinum wire of the thermoelement, which was also obtained by actual measurement. The wire, as the curve itself clearly shows, was considerably altered near the hot junction. *OK* is the thermoelectric power of the platinum-rhodium wire which formed the other branch of this element. *OK* is, therefore, the thermoelectric power which would have existed at the junction had there been no contamination. In order to represent graphically the product $\theta dH$, the coördinates should preferably be $\theta$ and $H$; that is, the thermoelectric power should be plotted as a function of temperature and not of length. The required change of coördinates is effected by the following device: The line *OB* is drawn with *B* equal to the ordinate of the maximum temperature on the diagram. The temperature curve is projected horizontally upon this line, *L*, *M*, *N* of the curve falling at *L'*, *M'*, *N'*. The abscissæ of *L'*, *M'*, *N'* are now proportional to their ordinates (since they lie on a straight line through the origin) and are, therefore, proportional to the tem-

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[1] $H$, as here used, is strictly the mean thermoelectric power, a function of the temperature interval.

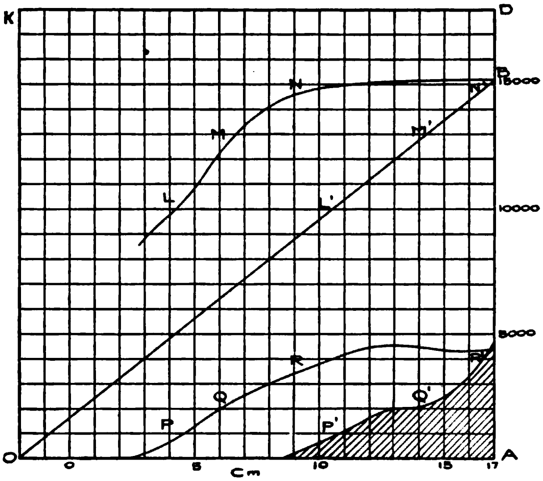

Fig. 1. Graphical method of computing the E.M.F. of an inhomogeneous element, applied to a platinum thermoelement in a resistance furnace. Upper curve, furnace temperature in microvolts (10 microvolts = approx. 1°), with depth in the furnace for abscissa; middle curve, thermoelectric power of the wire, arbitrary ordinate, same abscissa. Lower curve, same thermoelectric power, with temperature as abscissa. Total area, normal E.M.F., shaded area, error.

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[1] The furnace was of the type described by A. L. Day and E. T. Allen, PHYS. REV., 19, p. 184, 1904; Carnegie Institution Publication, No. 31, p. 25, 1905.

peratures. The thermoelectric power curve is next shifted horizontally so that all the abscissæ are altered by the same amount as in shifting the curve *L*, *M*, *N*. For instance, if *P*, *Q*, *R*, were originally under *L*, *M*, *N*, they will be moved to *P′*, *Q′*, *R′*, under *L′*, *M′*, *N′*. In practice, this shifting is easily done, and consists simply in taking with a pair of dividers *PP′* equal to *LL′*, *QQ′* equal to *MM′*, etc. The abscissæ of the curve *P′*, *Q′*, *R′*, being the same as those of *L′*, *M′*, *N′*, are likewise proportional to the temperatures. The curve *P′*, *Q′*, *R′*, therefore, has its abscissæ proportional to the temperature and its ordinates to the thermoelectric power. The area *OADK* represents the thermoelectromotive force which would be given by a thermoelement of homogeneous wires whose junction was at the temperature *OK*. The actual electromotive force is given by the area *O*, *P′*, *Q′*, *R′*, *D*, *K*, and the lowering of electromotive force due to contamination of the wire, by the approximately triangular shaded area *P′*, *Q′*, *R′*, *A*.

In this particular case, the effective thermoelectric power at the junction was about two thirds the normal, yet the reading of the thermoelement was lowered less than five per cent. The reason for this is, of course, that the contamination lay mainly in the region of uniform temperature, so that the maximum heat of the furnace extended out to a point where the difference in thermoelectric power between corresponding points of the two wires was much greater than at the junction. On the other hand, a small amount of contamination extending far from the junction evidently has a relatively great effect on the reading of the thermoelement—a point of importance in work with platinum thermoelements at high temperatures.

The reading of an inhomogeneous thermoelement is a function of all the temperatures throughout its length. In many cases where alterations in thermoelements have been reported, the effect observed was probaby due to change in the distribution of temperature along a really unaltered element.

Since the errors of thermoelements depend upon the intermediate temperatures, their constancy can be increased by increasing that of the temperature distribution between the junctions.[1] This is one of the ways in which the effect of an unavoidable inhomogeneity can be diminished. Of course, the element should then be calibrated for the particular temperature distribution with which it is to be used.[1]

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[1] Holborn and Day, Drud. Ann., 2, 538; Am. Journ. Sci., 10, 197, 1900.

On the other hand, the behavior of an element which has been used with a constant temperature gradient affords no criterion of the excellence of that element under less favorable conditions.

The errors due to inhomogeneity in thermoelements are sometimes, but incorrectly, spoken of as due to "Thomson currents." This doubtless arises from the fact that these errors are attributable to the middle and not to the ends of the wire. The Thomson effect, however, does not depend at all upon the heterogeneity of the wire, while the errors we have been discussing are directly due to it. Indeed, for most purposes it is convenient to think of an inhomogeneous theremoelement as composed of a number of short, weak elements in series.

*Thermoelectric Testing of Wires.* — The most satisfactory way to improve thermoelements is obviously to get rid of the inhomogeneity as far as possible, and such was the object mainly in view during the following work. In this attempt, the careful testing of the thermoelectric power of wires was important, either for study of their properties and behavior, or to control the selection and arrangement of the materials from which the thermoelements were made. Several types of thermoelectric wire testers were therefore made.

The thermoelectric properties of wires have usually been tested by moving some source of heat or cold along them — a Bunsen flame, for example, or a lump of ice.[2] This method has the advantage of simplicity, and usually shows the presence of inhomogeneity well enough. It seemed ill adapted to the quantitative work here described, for the following reason: In a thermoelement as ordinarily used, the electromotive force is not affected by any parts of the circuit which are at uniform temperature, but depends upon the difference in thermoelectric power of two wires, each of which passes from a hot to a cold region. Similarly, when a single wire is heated at one place, the portions which contribute to the resulting electromotive force are those which pass from hot to cold at the edges of the heated region, and this electromotive force, therefore, measures the difference in thermoelectric power of these two portions of wire through which the temperature gradients extend. If, now, the heating is by a Bunsen flame, the two gradients are very near each other. To get the difference between two distant portions of the wire many of the short-length observations must be combined. As the error of each measurement is usually large compared to the whole variation in the wire, the result obtained by adding a number of observations may easily be in error by more than its whole value. The differences between distant points of the wire, however, are precisely those which have the greatest effect on the reading of the element.

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[1] The deterioration of contaminated thermoelements is often given in degrees. Of course, any such statement is meaningless unless something is said or implied as to the conditions under which the element is to be read.

[2] Edwin H. Hall, L. L. Campbell and S. B. Serviss, Proc. Amer. Acad., 41, 559, 1906.

The common method was accordingly modified by disconnecting one end of the wire and completing the circuit through an auxiliary wire which touched the other somewhere within the heated portion. (Fig. 2.) The circuit then contained two temperature gradients, one on each wire, and by drawing the tested wire along, all portions of it could be compared with the same fixed portion of the other. A map of the whole wire could thus be made[1] and a comparison of any two portions would contain the errors of but two observations. The auxiliary wire should be of the same material as the one tested, since otherwise large electromotive forces are introduced, whose variation, even with slight fluctuations of temperature, may quite cover up the electro-motive forces due to the differences in thermoelectric power under investigation. The temperature gradient should be at least as short as the inhomogeneities to be located. This method succeeds best where the working difference in temperature is high, since the effect of temperature irregularities away from the testing point becomes less important. With an ordinary

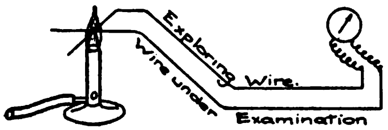

Fig. 2. Simple method of testing the thermoelectric height of a wire by means of a second exploring wire of the same material.

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[1] As in Fig. 5 (in which, however, the comparison was with a fixed portion of the same wire). This curve corresponds to the integral of any one of the curves given by Hall Campbell and Serviss (loc. cit.).

Bunsen burner as source of heat, it proved excellent for studying platinum wires. A temperature of 1000° can easily be reached and kept constant within 2 per cent. A somewhat greater variation will do no harm if the wires are of the same material. Since the heating is done by a rapid current of air, the temperature gradient is sharp.

When the testing is done at ordinary temperatures, on the other hand, differences of temperature at other places on the test wire may cause disturbances. It is then better to use two exploring wires, one on each side of the temperature gradient, as in Fig. 3. The only portion of the inhomogeneous tested wire in the circuit is then the part (2 cm. or less) actually under examination. Freedom from disturbing electromotive forces will then be obtained if (1) the temperatures are constant, or (2) the exploring wires are homegeneous. As both these conditions can be nearly secured, this method gives excellent results. Most of the wire testers which were tried were constructed on this principle and differed mainly in the method of maintaining the temperature gradient. Steam was the source of heat. Ice was tried for the lower temperature, but was abandoned because it caused a condensation of moisture and thus endangered the insulation.

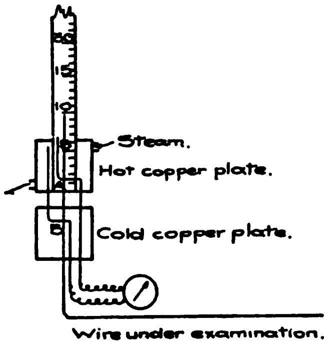

Fig. 3. Copper plate (dry) wire tester, using two exploring wires, making contact with the tested wire at *A* and *B*. The tested wire is drawn along the scale past the stationary exploring wires. Only two or three cm. of the tested wire is in circuit at one time, and all other wires exposed to temperature changes are of copper. A non-conducting pad covers the plates and wires when in use.

1. In the first form of tester, the wire ran from a hot to a cold globule of mercury. The results varied enormously with the condition of the surface of each metal. The temperature gradient was very sharp, but a sharp gradient was soon found to be seldom needed and to be obtainable by other methods; hence this form of tester was abandoned.

2. By putting a ring of lead pipe carrying steam in the top of a jar of kerosene, a sharp gradient was obtained on account of the slow conduction of heat downward from the warm layer which formed at

the top. The thermal contact of the fluid with the wire was of course excellent. This device seems to have advantages where only a few tests are needed and the construction of anything elaborate is therefore undesirable; but it cannot be made as convenient as several other forms, and the initial temperature difference steadily diminishes.

3. A small, square, wooden box was set in an oblong tin can and the whole filled with kerosene. Two bodies of kerosene were thus provided, separated by a thin vertical partition of wood. Pipes carrying steam and tap water maintained the two at different temperatures and a propeller in each caused rapid motion of the fluid at the place where the wires ran through the partition. This apparatus gave a very sharp gradient[1] and great freedom in arranging and connecting the wires. It was of value in several cases, but for ordinary work a more convenient arrangement is possible.

4. In the wire tester with which most of the work to be described was done, the temperature gradient was maintained by contact of the wires with hot and cold plates of copper (Fig. 3). These plates formed the tops of metal boxes, through which flowed steam and tap water respectively. They were covered with shellacked paper to insulate them from the tested wires. The wires were laid on the plates and covered with a weighted pad, which at once pressed them firmly against the plates, insured good contact with the exploring wires, and checked the escape of heat upward. The temperature distribution in the wires, secured merely by contact with a solid substance, is probably not very uniform or regular, but any variation due to this cause in the small electromotive forces measured was too minute to be noticed. In fact, the apparatus was originally constructed so as to admit of using kerosene to make better thermal contact, but experience showed that the use of this disagreeable fluid was not necessary. Of course, the temperature of the wire need not be that of the steam so long as it is constant.

If the wire to be tested is insulated, exploring wires can not be used. For such cases, various pieces of apparatus were employed whose common principle is shown in Fig. 4, where $E$ is an enclosure, maintained at a constant temperature by means of steam, through which runs the wire in such a way that any two portions of it may simultaneously be subjected to the temperature gradient at the edge of the enclosure, and thus compared directly with each other. If one point of the wire, *F*, is kept always at the edge, it can be compared in turn with all other points. The only essentials are that the temperature of the enclosure shall be constant and the length of wire within it capable of variation. It will not do, for example, to run the wire through a straight tube, since this requires heating a constant length of wire. The wire, however, if sufficiently flexible, can be doubled inside of a tube, when *F* and *M* will be near together at the same end. An apparatus of universal application is shown in Fig. 4. It consists simply of a long steam-heated metal case, flat on one side, against which lies the wire, covered by a thick pad of cloth. The temperature under such a pad is more uniform than that observed inside a steam-jacketed tube 14 mm. wide, and the adaptability of the method is obvious. This particular apparatus was not actually constructed, as the fine wires examined could be readily handled in tubes which we already had, but the constancy of temperature under a pad was measured carefully by means of a steam-heated varnish can. Such a can, or a flask, which can be set up almost at a moment's notice, makes a good substitute for the long metal case when the wire under examination is short.

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[1] Ninety-five per cent. of the temperature difference was within 1 cm. with platinum wires .6 mm. in diameter (No. 22).

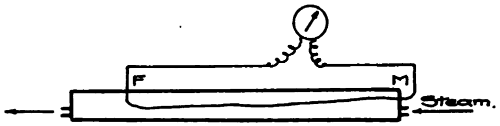

Fig. 4. Flat can wire tester. Adapted to insulated wires. The thermoelectric heights of any two portions, *F* and *M*, of the wire can be *directly* compared, and with almost no bending. A pad covers the wire when the test is made, or the wire may be inclosed between two similar cans.

Two types of thermoelements, one platin-rhodium, the other, constantan-copper, have been studied, with the result of improving considerably the accuracy of each.

1. *Platin-Rhodium Thermoelements.* — At the temperature of 1000° the platinum resistance thermometer begins to suffer a loss of accuracy. From that temperature up to 1600°, therefore, the thermoelement is the only satisfactory sensitive pyrometer available. Thermoelements made for high temperature work are now

tolerably familiar. Ordinarily they consist of a wire of very pure platinum, .6 mm. in diameter, joined by fusion to a wire of platinum alloyed with (10 per cent. of) rhodium or iridium. Couples containing iridium are the more sensitive at low temperatures. Their calibration curve is nearly linear. At higher temperatures, those alloyed with rhodium are nearly as sensitive and much more constant. They were the only ones studied. Connected to a voltmeter, these thermoelements form a direct-reading, convenient and accurate pyrometer of wide range. When read by means of a potentiometer, they are capable of much greater accuracy. One pair of elements has been carefully studied as far as 1000° and has never shown a disagreement greater than one half microvolt, corresponding to about $\frac{1}{20}$° at the higher temperatures, and other elements have usually given results almost equally good as high as 1500°.

The principal problem presented by our thermoelements was the rather unusual one of preventing a rapid and continuous alteration of the wires when in use.

It has long been known that the reading of platinum thermoelements and resistance thermometers is easily altered at high temperatures by contamination of the metal. As far as observed until recently, the trouble always occurred in a reducing atmosphere. Holborn and Wein[1] found that hydrogen alone had no effect, but in the presence of silicates it liberated silicon, which attacked the platinum. Reducing gases containing carbon were also believed to be deleterious to thermoelements, but I have not been able to find satisfactory experimental confirmation of this view. Holborn and Day[2] subsequently found that furnaces made of fresh or imperfectly burned clay gave trouble, which was attributed to the organic matter contained in the clay. The contaminated wires were usually restored by igniting at high temperatures in the air, though it was frequently necessary to cut off portions of the element on account of impurities which could not be driven out in this way. The danger of contamination in an oxidizing atmosphere seems hitherto to have been considered negligible.

When work was begun in this laboratory, the methods used by

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[1] Holborn and Wien, Wied. Ann., 56, 373, 379, 1895.

[2] Holborn and Day, loc. cit.

Holborn and Day at the Reichsanstalt were adopted, with some improvements calculated to adapt them for use at higher temperatures.[1] A platinum-iridium alloy replaced the platinum or nickel of the coils, and a new insulating material consisting mainly of magnesia was substituted for clay in the body of the furnaces. Rapid deterioration of the thermoelements at the higher temperatures was soon observed, the magnitude of which was altogether unexpected and for a long time defied explanation, as special precautions had been taken to avoid the presence of reducing matter in the furnaces. The possibilities of contamination through dissociation, electrolytic action, organic or ferruginous dust (both of which abounded in the laboratory), or the volatilization of iridium from the furnace coils, were all considered; but none of these explanations seemed to account for all the facts, and the further precautions which occurred to us, such as cleaning and ventilating the porcelain tubes surrounding the thermoelements, were without effect in remedying the trouble.

For a time, therefore, furnace work was conducted by means of a provisional arrangement. The working elements were used in their contaminated condition, but were compared frequently with standards which, being in the furnace only five or ten minutes each day, kept their values very well. The simplest way to compare the two thermoelements is, of course, to read both when at the same temperature. In an electric furnace of ordinary size, temperature gradients are so steep that the only satisfactory way to bring two junctions to the same temperature is to thrust both together into one of the porcelain tubes which are made for protecting thermoelements in furnaces. This can be done if each element has but one insulating capillary, leaving the other wire bare. If care is taken to keep the bare wires on opposite sides of the porcelain tube, the elements can be pushed down without crowding, and at the same time the capillary tubes will prevent the bare wires from coming in contact. No such contact has been observed in several hundred comparisons. The thermoelements thus located are read alternately and as rapidly as the galvanometer will allow. Change in the furnace temperature can easily be allowed for. Comparisons can also be made by putting one element after another into the same porcelain jacket, though not so well, since five minutes are required to attain temperature equilibrium after a cold element has been inserted in the jacket. Hence the furnace must previously be adjusted to constant temperature, which requires some time, and even then results are not very certain. Simultaneous readings of two elements in separate tubes are also unreliable at high temperatures, as equality of temperature can not be assured. In a furnace at 1400°, differences of 2° have been observed between similar tubes symmetrically placed and so close to each other as to be in contact through most of their length. By comparing two elements in two such tubes and then reversing and comparing again, the difference in temperature of the tubes can be eliminated and with excellent results. The conditions, however, must be such that the temperature difference remains constant.

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[1] Day and Allen, loc. cit.

The comparing of thermoelements has been of the greatest value in high temperature work. It may be used as a substitute for or check upon the tedious process of calibrating by means of metallic melting points; it affords a valuable control of the extensive extrapolation which is necessary above 1000°, and insures that results obtained with different elements at these higher temperatures shall be comparable among themselves; and it serves to indicate the first signs of deterioration. Applied to elements which are much contaminated, however, it has a disadvantage obvious in the light of the previous discussion (see p. 452), since the reading of the contaminated elements, being a function of the temperatures throughout the contaminated portions, varies with the condition of the furnace. In that work which we were forced to carry on for some months with contaminated elements, this difficulty was minimized by correcting the elements immediately after the temperature reading had been taken and in the same tube, so that the temperature gradient along the element might be as nearly as possible the same for both operations. The contaminated ends of the working element were also cut off as soon as they had fallen off 3 or 4°. By virtue of these precautions, measurements could, in favorable cases, be made to agree within .3° at 1400°. There was often, however, a good deal of uncertainty, which made the continual comparisons seem very irksome. We were finally driven to a consistent effort to get rid of the contamination altogether.

The systematic attack upon the problem began with an attempt to learn more of the actual condition of the contaminated elements. This study was begun by physical methods, the thermoelectromotive force of the wire furnishing a convenient and delicate means of investigation. Several of the wire testers described above were used, and contaminated elements were examined, centimeter by centimeter. The first day's work yielded results of importance and led to several surprises, in which conclusions derived from the experience of others and from our own occasional observations were found to be for the most part erroneous.

In the first place, the process ot igniting the elements to free them from impurity was found to be practically useless, being almost without effect upon the contamination with which we were dealing. This practice, borrowed from the Reichsanstalt, had not seemed satisfactory, but whenever special failures were noticed, these had been attributed to a lack of thoroughness in the heating process.

Second, the thermoelectric height due to the contamination of the platinum wires proved many times greater than had been supposed. Immediately adjacent to the junctions, it was sometimes half that of the rhodium alloy of the other wire. The amount of alteration had previously been inferred from the change in the reading of the whole element when in the furnace, and thus, as is evident from the discussion of Fig. 1, above, too low an estimate had been made.

Third, a similar discovery was made regarding the rhodium alloyed wires. Nothing whatever appears to have been published upon this point; their contamination is considerably less than that of the pure platinum, and was therefore probably overlooked. The contaminating material was commonly believed to be subject to some selective absorption by which the platinum alone was affected. The tests, however, showed that the rhodium wires gained in thermoelectromotive power on the average one-fifth as much as the platinum. This information was especially important. The contamination had been supposed to be due to mere traces of foreign matter whose minuteness made the task of discovering and subsequently excluding them appear exceedingly difficult. The amount of impurity taken up by the rhodium wires, however, was evidently comparable to the amount of alloy (10 per cent.) initially present in them. The contaminating materials, therefore, were present in measurable quantities, and the prospect of identifying and then avoiding them appeared decidedly encouraging.

For this task, again, the wire testers were invaluable. They were capable of detecting an amount of impurity far beyond the reach of chemical analysis, and could work upon wires less than 2 cm. long. By subjecting short pieces of pure platinum wire to various possible sources of contamination, one after another, information could be obtained rapidly and at slight expense. When pure platinum wire was heated in our furnaces at 1400°, contamination occurred regularly and certainly, After an hour at this temperature, the resulting thermoelectromotive power (measured at 100°) was about 4 per cent. of that of the ten per cent. rhodium wire. One-third of a per cent. could readily be detected. There was therefore no question as to the possibility of recognizing the presence of any source of contamination similar to that existing in our furnaces.

1. The first possibly contaminating materials investigated were reducing gases containing carbon. Wires were heated directly in a blast flame and electrically in illuminating gas and carbon monoxid, to various temperatures up to the melting point of platinum, but no contamination whatever could be found. In this particular, our results fail to confirm the observation made by Holborn and Wien that while the contaminating action of hydrogen is due to the liberation of silicon, carbon alone may contaminate thermoelements.[1] Carbon, like hydrogen, appears to act simply as a reducing agent, and is detrimental only in the presence of other material which yields contaminating products on reduction.

2. A pure platinum wire was then suspended in a furnace without the customary porcelain protecting tube. The usual amount of contamination occurred. The results with gas had shown that the impurities came from the materials of the furnace; this experiment showed also that they reached the wire in the form of vapor. Among the volatile materials in the furnaces, iridium (from the heating coils) was the immediate object of suspicion. Our furnaces when hot were known to be filled with iridium vapor, which con-

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[1] Loc. cit.

densed as a black deposit on the cooler portions of the furnace in quantities sufficient for chemical identification.

3. Further light on this subject was obtained through the kindness of Mr. George B. Hollister, of the Corning Glass Works, Corning, N. Y., who loaned us a thermoelement which had been in continuous use at 1400° for four months in a glass smelter, which was heated exclusively by gas. If iridium was really the cause of the contamination, this element might have been expected to remain unaltered. It showed contamination, though comparatively little, considering the length of time it had been in use. A striking peculiarity was, however, presented by the rhodium wire, whose thermoelectromotive height was not increased at all. The contamination of this element, therefore, was clearly due to a different cause from that of our own. Furthermore, the absence of contamination in the rhodium wire suggested that that wire itself probably furnished the only contaminating material to which the platinum wire could have been exposed. The properties of the two metals are such that if iridium vapor was capable of alloying platinum in an oxidizing atmosphere, rhodium would naturally be expected to produce a similar and smaller effect. Hence, in spite of the contaminated platinum wire, the condition of this element strengthened the belief that iridium was the impurity in our own thermoelements. One and one half per cent. of rhodium has since been found in the platinum wire of the Corning element by chemical analysis, but this result was not obtained until sometime afterward.

4. A direct test of the action of iridium was of course next in order. To make it, the platinum wire must first be heated in the absence of iridium. All our furnaces contained that metal, but a means of excluding its vapor was found in the use of glazed Marquardt tubes. These glazed tubes are not recommended for use above 1200°, but their deterioration at somewhat higher temperatures is very slow, and the one used in this work gave no indication of injury from overheating after five hours at 1500°. A platinum wire heated in this tube for an hour at about 1500° showed no contamination. When the experiment was repeated with a piece of iridium-alloyed furnace coil wire beside it in the same tube, there was contamination, and about as much as usually occurred in the furnace itself with the same time and temperature.

Platinum was therefore certain to become contaminated in the presence of iridium. Since, moreover, this change agreed in amount with that acquired in the furnace, and since porcelain, a silicate, caused no injury to the wire, the inference seemed justified that the non-metallic furnace materials had no share in producing the contamination, but that it was entirely due to iridium and rhodium.

5. Further confirmation of the above results by chemical analysis now seemed feasible and desirable. Dr. Eugene T. Allen, of this laboratory, undertook the analyses, both of a wire contaminated with iridium and of the one from the Corning Works, supposed to contain rhodium. In both cases the impurity sought was found in substantially the amount expected from the observed change in thermoelectric power. Dr. Allen's report follows.

*The Detection and Estimation of Iridium and Rhodium in Thermo-elements.* — For iridium, the method in its essential features was that of Deville and Stas. The platinum-iridium alloy is dissolved in ten times its weight of pure lead, by holding the two in contact for four hours or more at about 1000°. Most of the lead is then removed by dilute nitric acid and the spongy residue extracted with ten per cent. aqua regia. The iridium remains undissolved. Several test alloys prepared by fusing pure platinum and pure iridium (from Heraeus) with ten times their weight of lead, gave invariably high results, but when the lead was increased to twenty times the weight of the platinum metals, the result was satisfactory.

| | Taken. | Found. |
|---|---|---|
| Pure lead, | 10 + gr. | |
| " platinum, | 0.5024 gr. | |
| " iridium, | 0.0117 gr. iridium | .0121 gr. |

Iridium in the platinum wire of an old thermoelement.

| Taken. | Found. |
|---|---|
| 9 cm. platinum wire, 0.4913 gr. | Iridium, .0076 gr. = 1.54 per cent. |

The metal obtained gave the following tests characteristic of iridium :

1. Mixed with sodium chloride and heated in chlorine it slowly changed to the somewhat volatile, brown sodium iridium chloride which dissolved in water with a red brown color.

2. The solution in 1 gave with ammonium chloride the rather difficultly soluble, almost black ammonium iridium chloride.

3. On boiling with alcohol and caustic soda a blue solution of iridium trichloride was formed.

4. A small portion heated with ammonium nitrate and concentrated sulphuric acid gave a blue color.

The rhodium was estimated by the method of Deville and Stas, which consists in the solution of the metal (it should be previously rolled into thin ribbon) in aqua regia, precipitation of the bulk of the platinum by saturated ammonium chloride solution, separation of the rhodium with the remaining platinum from the filtrate by long boiling with ammonium formate, and final separation of the rhodium by fusing with acid potassium sulphate, from which it is precipitated in condition to weigh, by the action of ammonium formate. The method was tested on an alloy synthesized from pure platinum and the ten per cent. rhodium alloy of Heraeus.

| | Taken. | Found. |
|---|---|---|
| Pure platinum, | 0.4440 gr. | |
| 10% rhodium wire, | .0241 gr. | |
| ∴ rhodium = | .0024 gr. | rhodium — .0027 gr. |

The filtrate from the ammonium platinum chloride, amounting to perhaps 20 cm.$^3$, was decidedly pink, and the color of the potassium acid sulphate fusion when hot was claret, yellow when cold. On trial it was found that one mg. of rhodium (in the form of potassium rhodium chloride[1]) in 10 cm.$^3$ was distinctly pink.

Rhodium in the thermoelement.

| | |
|---|---|
| Taken — platinum wire of element, | .4484 gr. |
| rhodium found, | .0033 gr. |
| = | 0.73 per cent. |

The same color indications of rhodium were observed here in the filtrate from the ammonium platinum chloride and in the potassium acid sulphate fusion.

6. Although platinum wire was not injured in a gas flame, in the exhaust from a Fletcher gas furnace contamination occurred, as had, indeed, been expected. The cooler portions of the furnace

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[1] The author is indebted to Dr. W. F. Hillebrand for a sample of this rhodium salt.

top were covered with a deposit of ferric oxide, which was so distributed as to show that iron in some form had almost certainly been brought up from the furnace by the escaping gas, oxidized, and deposited there. It therefore seemed quite probable that iron vapor, as well as silicon,[1] may be a contaminating material in furnaces containing a reducing atmosphere. This was confirmed by heating platinum as usual, at 1500°, in a glazed porcelain tube with a few milligrams of iron wire. Contamination resulted, although the two wires were not in contact.

7. An investigation of the behavior of iron in an oxidizing atmosphere was suggested by this last result. Ferric oxide heated as usual in a glazed porcelain tube with (but not touching) a fragment of platinum wire, failed to produce any contamination; thus strengthening the conclusion that non-metallic furnace materials are harmless in an oxidizing atmosphere.

Platinum, then, is subject to contamination at high temperatures by the vapor of iridium and rhodium, even when these are present in small quantities. The impurity is only slightly diminished by ignition in air. Besides these metals, and gold and silver, there seems to be no contaminating agency which need be feared in an oxidizing atmosphere. Commercial platinum always contains iridium, and its use within the furnace must either be avoided, if thermoelements are to be kept constant, or else some protecting arrangement, such as glazed porcelain tubes, be used. Unglazed tubes, except in metal work, are valuable only as a mechanical support. In any case, contamination of the platinum from the rhodium wire will take place, although with relative slowness. Good elements, therefore, should preferably be exposed to high temperatures for as short periods as possible. A reference to Fig. 1 shows that platinum does not become contaminated by iridium vapor below about 900°.

Thermoelements alloyed with iridium are known to be less constant than those with rhodium, and the difference has usually been attributed to the loss of iridium by evaporation from the alloy. In the light of what precedes there can be little doubt that it is due rather to the absorption of some of the iridium vapor by the platinum wire. If this is so, iridium elements should be more constant if used so that the platinum and the alloyed wires were not close to each other. On inquiry, it was found that Drs. Waidner and Burgess, of the National Bureau of Standards, in this city, had actually observed that iridium elements kept their calibration better when stretched directly through the furnace than when doubled at the junctions as usual.

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[1] Shown to be a contaminating material by Holborn, Wien and Mylius. Holborn & Wien, loc. cit.

Beside chemical composition, the hardness of a metal affects its thermoelectromotive force, and the platinum thermoelements are liable to a temporary error from this source. New elements are usually hard from the drawing of the wire, sometimes reading as much as two per cent. high at room temperature. If they are not annealed before use, the softening of the heated portions produces inhomogeneities, which are also liable to continual change on further heating. The wire may also become hard during use from bending or other mechanical strains incident to handling, and also perhaps as a result of the brittleness (crystallization) which platinum attains when heated to moderately high temperatures — a point deserving further investigation. Fortunately, the annealing of platinum wires is very easy, on account of the absence of oxidation, so that the hardness of a platinum thermoelement need never be regarded as other than temporary. In this laboratory, only that part of the wire which is to be in or near the furnace is usually annealed. A wire of the usual size, .6 mm. in diameter, will carry 17 amperes when freely suspended, while 15 amperes is more than sufficient to soften it. There need be, therefore, no danger of melting off the wire.

The chemical purity of the original material is less under the user's control than most other causes of inhomogeneity. It is fortunate, therefore, that the chemical homogeneity of the best platinum elements now on the market is practically perfect. The platinum and rhodium wires of two thermoelements were tested throughout their length of 150 cm. at 1000° by means of a Bunsen burner, in the manner described above (p. 454). No effect due to inhomogeneity was found as great as the accidental errors of observation, which were about one-hundredth of one per cent. of the electromotive force of the element at that temperature. In ordinary use the temperature at any one point of the element would rarely vary 100° for the same temperature at the junction, and the error due to inhomogeneity would therefore not exceed .01°, which is considerably less than the usual error from other causes.

The last discussion suggests a point of some interest. The standard size of thermoelements (.6 mm.) was adopted after investigation by Holborn and Day, who found that finer wires did not give constant results. At that time, however, the contamination of platinum was not so well understood, nor the danger from hardening. It seems highly probable, therefore, considering the great homogeneity of thermoelement platinum, that considerably finer wires than .6 mm. would work perfectly well in very many cases. The main disadvantages would be the increased liability to contamination, and the greater danger from insufficient insulation, due to the higher resistance. Both these effects would decrease very rapidly with the temperature. The main advantages would be the lessened conductivity for heat and the reduced cost.

Any account of the present investigation would be incomplete which did not acknowledge its special indebtedness to the active interest of Dr. Arthur L. Day, of this laboratory.

II. *Copper Constantan Thermoelements.* — The second type of thermoelement investigated was of copper and constantan, and was intended for work at ordinary temperatures. The reasons for preferring a thermoelement to a resistance or mercury thermometer lay largely in the special conditions of the work for which they were to be used. The expectation of attaining greater ease and accuracy of reading than with a mercury thermometer has been abundantly confirmed.

The work of Hall, Campbell and Serviss,[1] and of Palmer[1] had apparently shown that an accuracy of .01°, for measurements up to 45°, could readily be obtained with commercial wire. Instead of a single thermoelement, five elements connected in series were used, enclosed side by side in a common tube, constituting what may perhaps be called a thermobattery. A double advantage was expected from this mode of construction: (1) The greater electromotive force made errors in the electric measurements less important, and (2) the accidental inhomogeneities in the wires would tend to neutralize each other. Insulated wire was, of course, needed, and copper was therefore substituted for the iron or steel commonly used. This change was considered an advantage, however, for another reason. Iron wire is notoriously uncertain in its thermoelectric properties, while copper is remarkably constant; hence, with wires of copper and constantan, there is only one-half the likelihood of trouble from inhomogeneity, and the electromotive force is still four-fifths as great as with constantan and iron. The constantan wire was No. 36 (.127 mm. diameter) obtained from the Driver-Harris Company, by whom it is sold under the trade name, "Advance." In order to control the accuracy of the results, two similar thermobatteries were made. Comparisons of these under various conditions showed that the readings were not constant, and that the trouble was probably due to inhomogeneity in the original material. An examination of some fresh wire from the same spool by means of a jacketed tube tester confirmed this suspicion. Three samples of wire, each 3 m. long, gave similar curves, one of which is shown in Fig. 5. The maximum variation is about .2 per cent. of the thermoelectromotive force against copper. This variation is evidently periodic. Mr. H. C. Dickinson, of the Bureau of Standards, in conversation, has mentioned finding inhomogeneities with a period of the same length, about 60 cm., in wire of a different size obtained from the same company. I am indebted to him for the suggestion that the periodicity of the inhomogeneity points strongly toward an origin in the annealing process, when the wire may have been in coils of 60 cm. circumference. It is inconceivable that the peculiar curve of Fig. 5 should itself be the result of chemical inhomogeneity, nor are there any other irregularities greater than .013 microvolt per degree which can be due to that cause. Probably the effect of chemical inhomogeneity is even less than that, and altogether negligible.

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[1] Loc. cit.

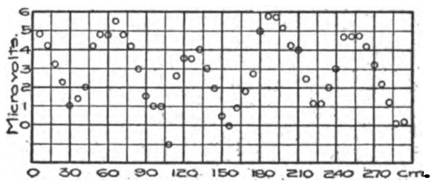

Fig. 5.

Better wire could, therefore, doubtless have been obtained by further search, but it seemed preferable to avoid delay by using that on hand, diminishing the effect of its irregularities by the method of construction. The device employed was the one already tried, of allowing the inhomogeneities to balance each other, except that instead of trusting to the chances of partial compensation among the numerous wires, the curve in Fig. 5 was used to select two lengths of wire which could be combined so that their variations were at every point nearly equal and opposite. The resultant thermoelectromotive power, as indicated by the curve, was then constant within .013 microvolt. The probability of error from inhomogeneity with the thermobatteries thus made can be estimated as follows: Whenever a thermoelement has received an individual calibration, the errors due to inhomogeneity depend, not upon the absolute values of the intermediate temperatures, but upon their variation from the condition prevailing during calibration. The results of the calibration will, therefore, include the effect of all temperatures which regularly vary with the junction, that is, of the temperatures of the portions near the junction, which are immersed in the bath with it. The variations of temperature which may accompany a given temperature at the junction are the only ones which can cause error. As the thermobattery here described was to be used with nearly constant immersion, the greatest variation of this sort was that of the portion exposed to the air, and was not greater than 20°. The maximum error was, therefore, 20 × .013, = (about) .25 microvolt, and since the thermoelectric power was 80 microvolts for a degree, this corresponded to an error of .003°. The result fully confirmed this estimate. Two such thermobatteries were made. Inclosed in the same tube they showed a permanent difference (which is not an error) of about .3 microvolt at 30°, which was about the limit of the sensitiveness of the galvanometer. The variation between the two was less than this, and altogether too small to measure. When both junctions of one were immersed in ice baths, the middle running through the air at about 30°, no variation from zero in the reading could be detected. With the two batteries in series, therefore, the error is not over .002°, and probably much less, as far as the batteries themselves are conerned.

These results are not markedly better than those reported by

Palmer, except for the increased sensitiveness gained by putting the elements in series. The method by which they were obtained, however, leaves the experimenter less dependent upon good fortune in getting originally homogeneous wire. Palmer does not appear to have considered the inhomogeneities of commercial wire at all important. The very experiment which is often used to investigate the quality of a thermoelement — that of reading it with both junctions in ice — he uses to show that the temperatures of the different ice baths were identical, and he does not mention inhomogeneity at all. His results, therefore, while they show something of the accuracy attainable with the thermoelement, appear to be misleading as to the ease with which that accuracy can ordinarily be obtained with commercial wire.[1] Their reproduction by another will be uncertain, if not improbable, without attention both to the quality and the treatment of the wire.

On the other hand, it should not be forgotten that the extreme refinement here considered is not always needed; sufficient accuracy for many kinds of work can usually be obtained with such simple precautions as are discussed immediately below.

The permanence of the thermobatteries seemed to depend npon three things. First, freedom from mechanical strain, the hardening effect of which is well known. Whether annealing is a satisfactory remedy in the case of constantan does not seem to be settled. With insulated wires it was, of course, out of the question.

Second, protection against chemical change, which in this case means oxidation. The effect of a layer of tarnish in altering the thermoelectric power of wires is also familiar. A number 22 constantan wire (.6 mm. in diameter) which had lain exposed to the air of a well ventilated laboratory for three months had its electromotive force against copper altered over .6 per cent.[2] This trouble can be corrected by scouring off the tarnish, but the restoration of the original electromotive force of the wire was not considered certain. Moreover, this remedy also was inapplicable to insulated wires.

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[1] It will not do to infer from Palmer's results even the probable homogeneity of commercial wire, since three of his elements (page 75) differ .1 per cent. among themselves, indicating that there was somewhere in the wire a variation in thermoelectric power at least half as great as that shown in Fig. 5. That amount of inhomogeneity would often produce errors considerably greater than those he actually found.

[2] Elements of constantan and other base metals, therefore, will not maintain their accuracy at temperatures high enough to cause oxidation.

Third, preservation of the insulation, which meant, practically, protection against moisture.

All these requirements could have been secured well enough in ways which would have left the middle portion of the wires reasonably flexible. But since, for the work in hand, rigidity was not inconvenient, it seemed better to avoid all possibility of trouble, and the elements were accordingly completely inclosed in suitably bent glass tubes.

The outside diameter of the tube inclosing the hot junction of both batteries is 3.3 mm. at the end. The time lag is 3 seconds in gently stirred water. The resistance of each is about 30 ohms.

The permanence of constantan elements can also be increased in another way. Wire is less liable to vary if initially in the condition to which use tends to bring it. Just as elements used at high temperatures, where they are certain to become annealed in part, should be annealed throughout before calibration, so those liable to be irregularly hardened in handling become immune toward that cause of inhomogeneity if thoroughly hardened in the first place. Of course, the hardening must be uniform, and the possibility of making it so seemed worth a brief investigation.

The small insulated constantan wire was easily hardened by working it back and forth over the square corner of a piece of wood. Wires thus treated, after being "aged" by heating to 100° for 15 minutes (a precaution whose necessity was immediately discovered) were tested for thermoelectric power. The total electromotive force against copper had increased .8 per cent or .33 microvolt per degree, but the greatest variation along the wire was less than the experimental error, which was about .013 microvolt per degree. This uniformity was not dependent on uniform working of the wire, as long as the hardening was thorough. The wires seemed to rapidly approach a constant condition. This would naturally be anticipated, and is essential if the method of hardening is to have much practical value. An important further consequence of it is that any variations in hardness originally present will disappear as the wire approaches the uniform condition. Hardening, therefore, supplies a method of securing initial homogeneity as well as of increasing the permanence of the element in use.

The degree of homogeneity shown to exist depended upon the experimental error in the method of testing. A more careful examination would probably show that the actual homogeneity is considerably greater than that already demonstrated. Further investigation of this question, however, while desirable, has seemed more appropriate to a laboratory not especially equipped for work at high temperatures. The original object of the present investigation was secured by the construction of the pair of enclosed thermoelements already described. For the method of hardening wires, enough seems to have been done in calling attention to its value, and showing that it is already capable of producing homogeneous thermoelements whose errors scarcely exceed those of the electrical apparatus by means of which they are likely to be read.

## SUMMARY.

1. The main source of error in thermoelements is inhomogeneity, by the removal of which, in most cases, far greater accuracy may be attained than has hitherto been realized.

2. The electromotive force of an inhomogeneous element equals $\int \theta dH$, where $\theta$ is temperature, and $H$, the thermoelectric power. This formula can be applied by a convenient graphical method. The errors due to inhomogeneity depend on the temperature distribution along the element also; a change in this distribution therefore produces the same result as a further alteration in the element. Such errors can be made to decrease indefinitely as the temperatures remote from the junctions of the element are made more constant.

3. Thermoelectric wire testers, of several easily constructed types, proved invaluable in these studies and in the making of thermoelements.

4. The effect of initial chemical inhomogeneity is practically negligible, as far as thermoelement work is concerned, in (Heraeus's) thermoelement platinum wires, in commercial copper, and, often if not always, in constantan.

5. The effect of physical inhomogeneity — that is the variation in hardness — in these wires can by no means be neglected. New wires are usually hard drawn. This hardness, as well as that which may result from bending, etc., can be quickly and effectually removed from platinum wires by annealing. In constantan, a

thorough hardening also produces uniformity and leaves the metal nearly free from liability to further change through handling.

6. Constantan and copper wires are apt to become chemically inhomogeneous through the formation of a film of oxide or other tarnish. Even at ordinary temperatures and in well ventilated rooms, an error from this cause amounting to as much as one half per cent. may easily develop within a few months. Cleaning off this film nearly, if not quite, restores the original calibration.

7. Platinum at high temperatures takes up impurities which diffuse into the wire. Carbon, illuminating gas, etc., produce this result only through their reducing action on other substances capable of injuring the platinum — of which iron (which reaches the platinum in the form of vapor) and silicon are perhaps the most important. In an oxidizing atmosphere, silicates and iron oxides are harmless, but contamination occurs above 900° from the presence in the hot furnace of small quantities of rhodium, and especially iridium, either pure or in alloys with platinum. All of these metals are somewhat volatile at high temperatures. The contaminating impurity can not be removed, but can be excluded by inclosure in glazed Marquardt porcelain, which, moreover, is fairly durable at 1500°.

8. Where the use of contaminated elements is necessary, fair accuracy can still be obtained by frequent comparison with standards under conditions such that the temperature gradient along the contaminated wire is always the same.

9. Frequent comparisons of platinum elements are always desirable in order to control the calibration and the unavoidable extrapolation.

10. Thermoelements of platinum-rhodium, and of constantan-copper, when used with proper precautions, have been found free from any error as great as .005 per cent. With the platinum, this amounts to less than one twentieth degree at 1000°; with constantan, to less than .002° for measurements up to 40°. Furthermore, this result with constantan was obtained with rather inferior wire, by uniting elements in series in such a way that the variations along the wires counteracted each other.

GEOPHYSICAL LABORATORY,
CARNEGIE INSTITUTION OF WASHINGTON, D. C.,
September 21, 1906.

# NOTE ON THE COMPARISON OF CAPACITIES.

By A. Trowbridge and A. H. Taylor.

IT has been pointed out by Rosa & Grover[1] that the capacity of a mica condenser is not the same for all rates of charge and discharge, and further, that in an alternating current circuit an absorbing condenser behaves as though it were an ideal condenser with non-inductive resistance in series, since the capacity current is out of phase with the electromotive force by less than 90°. For most mica condensers the angle by which the phase differs from quadrature lies in the interval $30''$ to $30'$ when the frequency is 100 cycles per second.

It may be easily shown that in the comparison of mica condensers of approximately equal capacities by an alternating current bridge method the error introduced by inequality of absorption may be neglected, and as the variation of the capacity of either condenser with the frequency of the alternating current is slight, a change in the ratio of the two capacities may reasonably be expected to be very slight.

The evidence would seem to point to the fact that more reliable comparisons could be made by use of an alternating current bridge than by the so-called bridge method, due to Maxwell, where no especial precautions are taken to remove the galvanometer from the circuit before an appreciable amount of the absorbed charge is released; for Zeleny[2] has recently shown that "the capacity of a mica condenser as determined by the ordinary direct deflection method is a variable quantity and a function of the period of the galvanometer," but that "the capacity determined from the free charge is independent of the period of the galvanometer and dependent on the condenser only."

It has seemed to the writers desirable to make a careful determination of the ratio of two similar condensers employing both the alternating current and the direct (variable) current, under the favorable conditions prescribed by Zeleny, with the purpose of ascertaining whether or not the two methods would give identical results to within the limit of error of about one hundredth of one per cent., which is easily attainable in such determinations.

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[1] Bulletin of the Bureau of Standards, No. 3, 1905.

[2] Phys. Rev., No. 2, 1906.

## Instruments and Method.

In order that the comparison might be carried out under as nearly similar conditions as possible in the cases of the alternating current and direct current circuits, the same resistance boxes were used in the same positions in both arrangements. These boxes were constructed of manganin wire by Otto Wolff and one of them had been certified by the Reichsanstalt as correct to one part in 10,000. By comparison the other boxes were found to be equally reliable.

The only essential respect in which the alternating current and direct current circuits differed was in the type of galvanometer used, but these were made as nearly similar as the limitations of the problem allowed.

It was thought best to use in both cases a differentially wound galvanometer, as such an instrument may be made practically free of inductance in the state of balance and hence may be shunted with non-inductive resistance with the certainty that the current will divide in inverse proportion to the ohmic resistances of shunt and coil.

The direct current differential galvanometer was a four coil astatic mirror instrument provided with a triple cylindrical soft iron shield to diminish the restoring force of the earth's field. The needles of the astatic system were eight in number and made of tungsten steel. The whole system weighed between four and five milligrams and was supported by a quartz fiber.

Each of the four coils was shaped so as to give nearly maximum field strength for given resistance and was wound with No. 40 silk-insulated copper wire. In winding these coils two strands of the wire were spun around each other and this double wire wound on a frame. Frame and double coil were immersed in hot carnoba wax until the air was expelled from the insulation. When cool the double coil was slipped off the frame, as it was sufficiently hard to be mounted without a frame in its place in the galvanometer. Each of the four coils of the galvanometer thus consisted of two sets of windings the resistances and inductances of which differed but very slightly. Care was taken in mounting these coils in the galvanometer to pair them off, so that the total resistance of each set of four coils in series was as nearly alike as possible. When the coils were in position the galvanometer consisted of four coils each of which was double, so that there were two circuits through the galvanometer practically coincident along their whole length.

Each of these circuits had a resistance of about 134 ohms and with either set of windings the current sensibility of the instrument as it was finally used was $10^{-9}$ amperes per mm. deflection at $1^{m}$ scale distance.

By sending the same current through the two sets of windings so that their magnetic effects on the needle system were in opposition, it was found that if this current were less than $10^{-5}$ amperes there was no noticeable deflection of the needle. Thus the two systems of windings were symmetrical as regards their magnetic fields, and hence as regards their self-inductions, to within one part in 10,000 which was regarded as satisfactory considering that the effect of a slight asymmetry could be eliminated when it came to the comparison of capacities by the simple expedient of exchanging the two windings. The following scheme of connection will illustrate the method adopted for the comparison of capacities by means of the differential galvanometer.

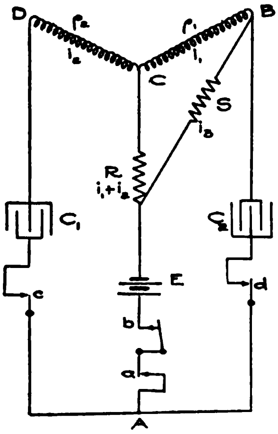

Fig. 1.

$\rho_1$ and $\rho_2$ represent the windings of the galvanometer (shown separate in the figure but really coincident and connected so as to oppose in their magnetic effect on the needle system) $C_1$ and $C_2$ the capacities to be compared; $R$ and $S$ resistance boxes accurate to 1 in 10,000; $a$, $b$, $c$, $d$, are keys which are thrown from left to right (in the figure) by a pendulum in the order *a–b* and then *c* and *d* together. The position of the keys could be varied so as to vary the intervals of time between the falling of the keys. It will be seen from the figure that the circuit is made as the key *a* falls — is broken later by the falling of the key *b* and an instant later the keys *c* and *d* break the circuit *ABCDA* through both condensers and the galvanometer coils in series. As the time between the falling of key *b* and keys *c* and *d* was made extremely small (roughly estimated at a few thousandths of a second) this pendulum apparatus secures the charging of the condenser $C_1$ and $C_2$ by a common electromotive force *E*, through the resistances in the branches which respectively contain them.

Calling $i_1$ and $i_2$ the instantaneous values of the currents through $\rho_1$ and $\rho_2$ the galvanometer will show no deflection on charging the condensers if $i_1 = i_2$.

But $(i_1 + i_2)R + i_1\rho_1 = i_3S$ and

$$i_1\rho_1 + \frac{1}{C_1}\int (i_1 + i_3)dt = i_2\rho_2 + \frac{1}{C_2}\int i_2 dt,$$

but if $i_1$ is to equal $i_2$ ($\rho_1$ being equal to $\rho_2$) then

$$\frac{1}{C_1}(i_1 + i_3) = \frac{1}{C_2}i_2,$$

but

$$i_3 = \frac{(i_1 + i_2)R + i_1\rho_1}{S'}.$$

$$\therefore \frac{1}{SC_1}(S\rho_2 + R\rho_2 + \rho_1\rho_2 + R\rho_1) = \frac{\rho_1}{C_2}$$

or

$$\frac{C_1}{C_2} = \frac{S + \rho + 2R}{S} \qquad \text{Eq. } B$$

since $\rho_1 = \rho_2 = \rho$.

It was found that the balance was not disturbed by changing the relative positions of the keys *a* and *b* which shows that the balance point was unaffected by any existing difference in absorption of the two condensers.

The alternating current galvanometer was of the D'Arsonval type as used by Terry[1] in determining the temperature coefficient of a capacity. In order to make it differential in its action the coil was made of two symmetrical windings of No. 40 wire braided together and with a common terminal leading to the phosphor-bronze upper suspension. There were two lower suspensions of very fine phosphor-bronze attached to the two windings. This method of connection (the use of a common terminal) necessitated an extra half turn on one winding. This half turn could be shifted across the face of the coil until the magnetic effects of the two windings, as tested with direct currents, were balanced to within one part in ten thousand. When used differentially the inductances of the windings were very nearly zero. The field of the galvanometer was of laminated iron with a winding designed to be connected directly to a 110-volt 60-cycle circuit.

This galvanometer may be substituted for the differential telephone or transformer with a great gain in sensibility and in symmetry of windings. For the comparison of capacities the method of connection is that shown in Fig. 2.

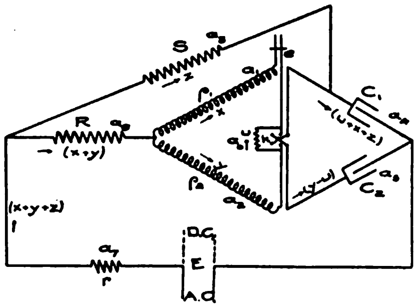

Fig. 2.

The windings $\rho_1$ and $\rho_2$ are shown separated. The slide wire $l$ serves to bring the resistances $\rho_1$ and $\rho_2$ very nearly to equality. This is determined by a direct current balance with the capacities $C_1$ and $C_2$ cut out, and with direct current on the galvanometer field, which is not shown in the sketch. A commutator serves to exchange $C_1$ and $C_2$ for the elimination of errors due to asymmetry. These errors were very small. A double pole double throw switch serves to throw 110 volts A.C. or 2 volts D.C. on the circuit. The control resistance $K$ functions exactly as it would in the case of an ordinary A.C. galvanometer, not wound differentially, (Terry. loc. cit.) and hence by its adjustment the coil can be given any desired degree of stability in the alternating field. With respect to the E.M.F. induced in the windings by the alternating field, the resistance $K$ is in series with both windings acting together; but with respect to the measuring current, at the moment of balance $K$ is connected at two points whose potentials are the same. At the moment of balance $K$ carries no part of the measuring current and hence does not necessarily need to be considered in the equation of balance.

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[1] Physical Review, September, 1905.

This arrangement differs markedly from that used by Trowbridge[1] in the comparison of capacities with the differential transformer only in the use of the resistance $R$. This gives far more effectiveness to the shunt $S$, which in turn does not have to be so small when very unequal capacities are compared. Moreover, the sensibility is very nearly the same with a 5:1 ratio of capacities as with an equality balance.

The theory of the network of conductors is given below where $u$, $x$, $y$, $z$, etc., represent the alternating currents in the various branches, $a_0$, $a_1$, etc., the complex expressions for the impedances and $E$ the impressed alternating electromotive force.

Since the self inductions of the coils $\rho_1$ and $\rho_2$ of the galvanometer at the instant of balance are just offset by the mutual induction between them as the currents are equal and oppositely directed it is not necessary to include these inductances in the impedances $a_1$ and $a_2$.

$$a_1 = \rho_1; \qquad a_3 = \frac{1}{jc_2\omega}; \qquad a_5 = S;$$

$$a_2 = \rho_2 \qquad\qquad\qquad\qquad a_6 = R;$$

$$a_0 = K; \qquad a_4 = \frac{1}{jc_1\omega}; \qquad a_7 = r.$$

Applying Kirchoff's laws,

$$ya_2 + ua_0 - xa_1 = 0,$$

$$(u + x + z)a_4 + ua_0 - (y - u)a_3 = 0,$$

$$(x + y)a_6 + xa_1 - za_5 = 0,$$

$$(x + y + z)a_7 + za_5 + (u + x + z)a_4 = E.$$

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[1] PHYSICAL REVIEW, February, 1905.

Rearranging terms,

$$a_0 u - a_1 x + a_2 y + oz = 0,$$

$$(a_0 + a_3 + a_4)u + a_4 x - a_3 y + a_4 z = 0,$$

$$ou + (a_1 + a_6)x + a_6 y - a_5 z = 0,$$

$$a_4 u + (a_4 + a_7)x + a_7 y + (a_4 + a_5 + a_7)z = E.$$

$$u = \frac{1}{\Delta}\begin{vmatrix} O & -a_1 & +a_2 & O \\ O & +a_4 & -a_3 & +a_4 \\ O & +(a_1 + a_6) & +a_6 & -a_5 \\ E & +(a_4 + a_7) & +a_7 & +(a_4 + a_5 + a_7) \end{vmatrix}$$

$$= \frac{E}{\Delta}\begin{vmatrix} -a_1 & +a_2 & O \\ +a_4 & -a_3 & +a_4 \\ +(a_1 + a_6) & +a_6 & -a_5 \end{vmatrix},$$

$$u = \frac{E}{\Delta}\left[a_1(a_4 a_6 + a_2 a_4 - a_3 a_5) + a_2 a_4(a_5 + a_6)\right],$$

$$x = \frac{1}{\Delta}\begin{vmatrix} +a_0 & O & +a_2 & O \\ +(a_0 + a_3 + a_4) & O & -a_3 & +a_4 \\ O & O & +a_6 & -a_5 \\ +a_4 & E & +a_7 & +(a_4 + a_5 + a_7) \end{vmatrix}.$$

$$= -\frac{E}{\Delta}\begin{vmatrix} a_0 & a_2 & O \\ (a_0 + a_3 + a_4) & -a_3 & +a_4 \\ O & +a_6 & -a_5 \end{vmatrix}$$

$$\therefore x = -\frac{E}{\Delta}(a_0 a_3 a_5 + a_2 a_5(a_0 + a_3 + a_4) - a_0 a_4 a_6)$$

$$y = \frac{1}{\Delta}\begin{vmatrix} a_0 & -a_1 & O & O \\ (a_0 + a_3 + a_4) & a_4 & O & a_4 \\ O & (a_1 + a_6) & O & -a_5 \\ a_4 & (a_4 + a_7) & E & (a_4 + a_5 + a_7) \end{vmatrix}$$

$$= +\frac{E}{\Delta}\begin{vmatrix} a_0 & -a_1 & 0 \\ (a_0 + a_3 + a_4) & a_4 & a_4 \\ 0 & (a_1 + a_6) & -a_5 \end{vmatrix}$$

$$y = +\frac{E}{\Delta}\left[-a_0a_4a_5 - a_1a_5(a_0 + a_3 + a_4) - a_0a_4(a_1 + a_6)\right].$$

The condition of balance is $x = y$ and $a_1$ is made $= a_2 = a$,

$$a_0a_3a_5 + a_2a_5(a_0 + a_3 + a_4) - a_0a_4a_6$$
$$= + a_1a_5(a_0 + a_3 + a_4) + a_0a_4a_5 + a_0a_4(a_1 + a_6)$$

$$\therefore \frac{a_3}{a_4} = \frac{a_5 + a + 2a_6}{a_5} \qquad \text{Eq. } A$$

$$\text{or } \frac{C_1}{C_2} = \frac{S + \rho + 2R}{S} \qquad \text{Eq. } B$$

but $u = \frac{E}{\Delta}\left[a(a_4a_6 + aa_4 - a_3a_5) + aa_4(a_5 + a_6)\right]$

$$= \frac{Ea}{\Delta}\left[a_4(2a_6 + a + a_5) - a_3a_5\right]$$

but from Eq. $A$, $a_3a_5 = a_4(a_5 + a + 2a_6)$

$\therefore$ when $x = y$ ($a_1$ being equal to $a_2$)

$u = 0$ or no current from the bridge flows through the resistance $K$.

Under these conditions Eq $B$ gives the value for the ratio of the capacities.

In obtaining the balance both with the alternating current and the direct current circuits, the practice was to exchange the positions of $C_1$ and $C_2$ and so obtain a mean value of $C_1/C_2$ which was free from error due to any slight asymmetry in the apparatus. Of course, the resistance $S$ had always to shunt the circuit through the greater capacity.

The rôle played by the resistance $R$ is evident from the equations or from the diagrams. Its presence slightly reduces the sensibility but on the other hand it makes an accurate knowledge of the resistance $\rho$ less important than as though $R$ were suppressed. This is a great advantage since the galvanometer coils $\rho$ consist of fine copper wire the resistances of which depend to a considerable extent on the temperature. Moreover, as has been mentioned above, the presence of the resistance $R$ makes the method applicable to the comparison of capacities whose ratio is as great as ten to one.

The above mathematical treatment is of course, applicable to the comparison of inductances. In this case the formula inverts; that is

$$\frac{L_1}{L_2}=\frac{S}{S+2R+\rho}.$$

In order to avoid taking accurate account of the temperature of the two capacities, we compared the two halves of a subdivided Elliot condenser of one microfarad capacity.

The comparison was made by means of a third Elliot condenser of about one-half microfarad capacity. Furthermore, the work was carried on in a basement room where the variation of temperature did not exceed 7° C., so that on the whole the error introduced by variations of temperature was probably negligible. The formulæ $B$ and $B'$ modify as follows when the ratio $C_1 : C_2$ is obtained by means of the third capacity $C_3$ which is smaller than either $C_1$ or $C_2$.

$$\frac{C_1}{C_3}=\frac{S_1+2R_1+\rho}{S_1} \text{ and } \frac{C_2}{C_3}=\frac{S_2+2R+\rho}{S_2}.$$

$$\therefore \left(\frac{C_1}{C_2}\right)=\frac{S_1+2R_1+\rho}{S_2+2R_2+\rho}\times\frac{S_2}{S_1}.$$

When the positions of $C_1$ and $C_2$ are exchanged,

$$\left(\frac{C_1}{C_2}\right)'=\frac{S_1'+2R_1+\rho}{S_2'+2R_2+\rho}\times\frac{S_2'}{S_1'}.$$

It will be seen from Table I. that the observations were taken over a period of about six weeks. They are recorded in the order in which they were taken beginning on April 11 for the comparisons by variable currents, and on April 13 for the comparisons by alternating currents. No observations were discarded, although some of the earlier observations with the alternating current galvanometer were not taken so carefully as were the later ones.

## TABLE I.

*Comparison by Direct Currents.*

| Date. | $R=R_2$ | $S_1$ | $S_1'$ | $S_2$ | $S_2'$ | $\frac{C_1}{C_2}$ | $\left(\frac{C_1}{C_2}\right)'$ | Mean $\frac{C_1}{C_2}$ |
|---|---|---|---|---|---|---|---|---|
| Apr. 11 | 0 | 14,100 | 14,700 | 8,300 | 8,500 | .9935 | .9935 | .99350 |
| " 13 | 0 | 14,650 | 11,950 | 8,500 | 7,600 | .9935 | .9936 | .99355 |
| " 15 | 0 | 15,900 | 13,000 | 9,000 | 7,900 | .9936 | .9935 | .99355 |
| " 17 | 0 | 16,050 | 13,000 | 9,000 | 7,950 | .9936 | .9936 | .99360 |
| " 22 | 0 | 14,700 | 12,000 | 8,600 | 7,600 | .9936 | .9936 | .99360 |
| " 22 | 0 | 14,800 | 12,050 | 8,650 | 7,600 | .9937 | .9936 | .99365 |
| " 23 | 380 | 97,500 | 80,500 | 57,700 | 51,600 | .9937 | .9939 | .99380 |
| " 23 | 380 | 100,000 | 82,000 | 59,000 | 52,000 | .9939 | .9938 | .99385 |
| " 23 | 300 | 84,000 | 68,200 | 48,700 | 43,200 | .9937 | .9939 | .99380 |
| " 24 | 200 | 61,000 | 50,000 | 35,200 | 31,200 | .9936 | .9937 | .99365 |
| " 24 | 150 | 50,500 | 41,500 | 29,200 | 25,500 | .9938 | .9936 | .99370 |
| " 25 | 100 | 42,700 | 33,500 | 23,400 | 20,400 | .9937 | .9936 | .99365 |
| " 25 | 33 | 25,300 | 20,100 | 13,960 | 12,150 | .9936 | .9936 | .99360 |
| " 25 | 333 | 101,000 | 80,700 | 55,200 | 48,700 | .9936 | .9935 | .99355 |
| " 25 | 333 | 100,900 | 80,500 | 55,300 | 48,400 | .9936 | .9935 | .99355 |
| May 27 | 33 | 23,200 | 17,940 | 13,200 | 11,300 | .9936 | .9936 | .99360 |
|  |  |  |  |  |  |  |  | Average, .99364 |

*Comparison by Alternating Currents.*

| Date. | $R_1=R_2$ | $S_1=S_1'$ | $S_2=S_2'$ | $\frac{C_1}{C_2}$ |
|---|---|---|---|---|
| Apr. 13 | 1.5 | 17,800 | 10,830 | .99400 |
| " 13 | 1.5 | 16,768 | 10,393 | .99403 |
| " 14 | 1.5 | 16,883 | 10,273 | .99363 |
| " 14 | 1.5 | 17,150 | 10,425 | .99375 |
| " 14 | 1.5 | 19,600 | 11,275 | .99372 |
| " 14 | 1.5 | 20,169 | 11,619 | .99378 |
| " 14 | 1.5 | 19,500 | 11,399 | .99372 |
| " 26 | 1.5 | 18,475 | 10,975 | .99374 |
| " 26 | 151.5 | 50,075 | 29,475 | .99357 |
| " 27 | 151.5 | 50,700 | 29,850 | .99369 |
| " 27 | 151.5 | 52,100 | 31,175 | .99384 |
| " 27 | 151.5 | 50,000 | 29,750 | .99370 |
| " 27 | 201.5 | 61,650 | 36,500 | .99373 |
| May 25 | 1.5 | 18,204 | 10,600 | .99349 |
| " 25 | 1.5 | 18,110 | 10,650 | .99351 |
|  |  |  |  | Average, .99373 |

The general averages by the two methods agree to within nine parts in one hundred thousand. Had these averages been made excluding the first few observations, of which we are a little uncertain, they would have been considerably more concordant.

As the check upon the accuracy of the methods we divided the capacity $C_2$ into two parts of approximately .25 microfarads each, which we will call $C_4$ and $C_5$. By comparison with direct currents we determined $C_4/C_2$ and $C_5/C_2$ using the above mentioned third capacity $C_3$. The sum of these ratios should equal $C_1/C_2$, since $C_4 + C_5 = C_1$. Owing to certain discrepancies which appeared in this portion of the work with the comparison by alternating currents, we shortened the calculations for that method by determining simply $C_4/C_3$ and $C_5/C_3$, having previously determined $C_1/C_3$ which should therefore equal $C_4/C_3 + C_5/C_3$. The value of $C_1/C_3$ as determined from several averages was 0.98490.

### TABLE II.

*Comparisons by Direct Currents.*

| Date. | $\frac{C_4}{C_2}$ | $\frac{C_5}{C_2}$ | $\frac{C_4}{C_2} + \frac{C_5}{C_2}$ | Difference. |
|---|---|---|---|---|
| April 26 | .49623 | .49738 | .99361 | .00003 |
| May 29 | .49616 | .49736 | .99352 | .00012 |
| May 30 | .49621 | .49736 | .99357 | .00007 |

*Comparisons by Alternating Currents.*

| Date. | $\frac{C_4}{C_3}$ | $\frac{C_5}{C_3}$ | $\frac{C_4}{C_3} + \frac{C_5}{C_3}$ | Difference. |
|---|---|---|---|---|
| May 28 | .49828 | .49910 | .99738 | .01248 |
| May 28 | .49838 | .49914 | .99752 | .01262 |

It will be seen that for direct currents the agreement is satisfactory, since the differences between $C_4/C_2 + C_5/C_2$ and $C_1/C_2$ (average from Table I.) are small. The corresponding differences in the case of alternating currents are very large. In order to investigate the cause of these discrepancies another series of observations was taken, of which Table III. is a summary.

### TABLE III.

| Date. | $R_1$ | $R_2$ | $R_3$ | $S_1$ | $S_2$ | $S_3$ | $\frac{C_1}{C_3}$ | $\frac{C_2}{C_3}$ | Calc. $\frac{C_1}{C_3} + \frac{C_2}{C_3}$ | Obs. $\frac{C_1 + C_2}{C_3}$ | Diff. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| June 28 | 1.5 | 1.5 | 471.5 | 18,125 | 10,885 | 1,084.3 | 1.0092 | 1.0153 | 2.0245 | 2.0218 | .0027 |
| " 29 | 1.5 | 1.5 | 471.5 | 18,395 | 11,010 | 1,083.5 | 1.0092 | 1.0153 | 2.0245 | 2.0221 | .0023 |
| May 29 | 301.5 | 501.5 | 9001.5 | 84,750 | 76,200 | 18,080.0 | 1.0091 | 1.0153 | 2.0244 | 2.0134 | .0110 |

The two halves of the subdivided Elliot condenser, $C_1$ and $C_2$ were compared with $C_3$.

Then the whole of the subdivided condenser, $C_1 + C_2$, was compared with $C_3$.

The results do not check. This was found to be due to distributed capacity in the Wolff box $R$. An inspection of Table III. shows that consistent values for $C_1/C_3$ and $C_2/C_3$ are obtained with values of $R$ varying from 1.5 ohms (the resistance of the upper galvanometer suspension) to 501.5 ohms. A larger variation of $R$ for these ratios is impossible because of the enormous values of $S$ which would accompany high values of $R$. However, when obtaining $(C_1 + C_2)/C_3$ which is nearly a 2:1 ratio, very large values of $R$ can be used.

It will be seen from Table III that the value of $(C_1 + C_2)/C_3$ is very different when $R_3 = 9001.5$ and when $R_3 = 471.5$. This shows the effect of distributed capacity in $R$ when it is made up of a few coils of high resistance. The difference between computed and observed values of $(C_1 + C_2)/C_3$ increases to nearly five times its previous value. In order to test this point still further a regular capacity bridge was set up (Carhart & Patterson's Electrical Meas.) and it was found that when Wolff boxes were used in the bridge arms a perfect telephonic balance was impossible, on account of distributed capacity in the coils of these boxes.

The position of balance as indicated by a minimum sound in a telephone, or as indicated by an alternating current galvanometer was dependent upon whether the bridge arms consisted of a few high resistance coils or a large number of low ones of exactly the same ohmic resistance. This must be due to the greater distributed capacity in the high resistance coils.

A second curious effect was that a coil possessing distributed capacity, such as a 5,000 ohm coil in a Wolff box, *inserted entirely outside of the bridge circuit*, would affect the point of balance. This may be due to modification of the wave-form by this external distributed capacity, making overtones more pronounced, and thus rendering the distributed capacity in the bridge more effective. This effect was not noticeable unless there was distributed capacity in the bridge as well as in the external circuit.

Both of these effects were far less pronounced when manganin boxes of our own construction were substituted for the Wolff boxes. The coils in the Wolff boxes were wound on brass cylinders, which is an arrangement quite favorable for distributed capacity, while the coils in our own boxes were wound on wooden coils.

Unfortunately these boxes were accurate only to 0.1 per cent., and hence in using these boxes we obtained a check only to within that degree of accuracy. It seems quite clear, however, that the distributed capacity in large values of *R*, which carries the main current through both capacities, was responsible for the discrepancies noted in the alternating current comparisons.

Moreover, it is quite evident that boxes in which the coils are wound on brass cores, giving considerable distributed capacity are not to be depended on for alternating current measurements of more than moderate precision.

The applied voltage used in the comparisons by means of the differential alternating current galvanometer was varied from 10 to 110 volts at 60 cycles, with no appreciable effect on the results. Hence the varying electrostatic attraction between the condenser plates does not affect the ratio of the parts of the condenser.

A number of tests were made to determine whether distributed capacity in *S* had any influence on the results. The resistances *S* were built up first of a few high resistance coils and then of a number of small resistance coils of the same sum total ohmic resistance. No influence upon the results could be detected.

The shunt *S* carries in most cases so small a current that it was not expected that distributed capacity in it would be troublesome. We have, therefore, reason to believe that the results reported in Table I. are free from the errors due to distributed capacity, since *R* was small in all cases.

This paper may be summarized as follows:

1. A new circuit for the comparison of capacities and of inductances has been devised, which is more nearly free from errors due to distributed capacity than is the regular Maxwell bridge.

2. Within the limit of error, that is one ten-thousandth, it has been established that the ratio of two good mica condensers is the same, whether compared by direct or by alternating currents, pro-

vided that proper precautions be taken to eliminate the effect of absorption.

3. It has been shown that distributed capacity in high-grade resistance boxes whose coils have brass cores causes a serious error in alternating current measurements; an error which may be much reduced by using boxes whose coils are wound on wooden cores.

MADISON, WIS.,
July, 1906.

# AN IMPROVED METHOD OF MEASURING THE INFRA-RED DISPERSION OF MAGNETIC ROTATION; AND THE MAGNETIC ROTATORY DISPERSION OF WATER.

By L. R. Ingersoll.

IN a previous article[1] the writer described a bolometric method of measuring the electromagnetic rotation of the plane of polarization of infra-red radiations, if of not too long wave-length. This enabled the determination of the variation of magnetic rotation with wave-length — or the magnetic rotatory dispersion — for a spectral region several times as large in extent as that which could be explored by the customary visual methods. But measurements were difficult, and the several sources of error and rather large corrections to be applied, necessarily detracted somewhat from the certainty of the result.

During the past year, however, a number of radical changes have been introduced, which not only remove in great part the above defects, but also lend to the bolometric method possibilities for sensitiveness in the detection and measurement of minute rotations, considerably exceeding those of visual methods of observation. Hence, as it is believed that the advantage appeals to investigators of making a more thorough study of the magnetic rotatory dispersion of a large class of substances, this improved bolometric method of measurement is described. Results are also given of measurements by its use, of the magnetic rotatory dispersion of water.

The fundamental principle is as already described,[2] and is essentially that due to De la Provostaye and Desains.[3] Light passes in succession through a polarizing agent, through the rotating substance in a magnetic field, and through an analyzer, whose principal plane makes an angle of 45° with that of the polarizer. Any rotation of the plane of polarization will cause an increase or diminution of intensity of the light transmitted by the analyzer, which may be measured bolometrically, and for any desired wave-length if the beam is dispersed.

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[1] Phil. Mag. (6), 61, p. 41, January, 1906.

[2] Loc. cit.

[3] Ann. Chim. Phys. (3), XXVII., p. 32, 1849.

The practical difficulty which must be encountered is that small and unavoidable variations in the intensity of the light source may be falsely interpreted as rotations, and may indeed mask entirely the true effect if it is small. It appeared that it might be possible to overcome this difficulty by utilizing two equal beams from the same source of light, and having them fall eventually on two bolometers, so connected that their currents opposed each other at the galvanometer. For then any variation of intensity of the source would affect both beams equally and produce no resultant deflection, while if only one of the beams was polarized and made to pass through the magnetic field, it alone would suffer changes of intensity due to rotation, and the angle of rotation could be measured as readily as before.

A large number of trials have demonstrated the possibility of compensating in this way for variations of the source, but it has been found that for best results, the two beams should be as nearly identically similar as possible, and that instead of two bolometers, the two strips of a single bolometer may be used to advantage. To fulfill these conditions the following arrangement has been adopted, the general disposition of magnet and mirror system being as before, and as indicated in the diagram of the previous paper.

Light from a Nernst glower, after reflection from a concave mirror and passage through a double image prism and down the axis of the electromagnet, is brought to a focus between the pole-pieces. Only the direct, and therefore achromatic image from the prism is used, hence this prism might be replaced by a Nicol, although the latter, being longer, would cause more absorption. A second mirror converges the beam, after passing through a second double image prism, on a Vierordt double slit. The two images of the source falling vertically above one another on the two halves of the slit, form, after passing through the spectrometer, two slightly separated, and, with the exception of the azimuths of polarization, entirely similar spectra. These are received on the two strips of a bolometer, so constructed that the strips instead of being side by side, lie vertically over one another. The intensity of either spectrum for any given wave-length may thus be measured by shuttering either half of the slit, — or any relative change of intensity. This last is due to rotation, for, since the plane of polarization of the radiation as it passes between the poles of the magnet makes an angle of 45° with each of the two planes of transmission of the analyzing double image prism, any rotation will cause a diminution of intensity of one image on the slit and a corresponding increase in the other. This change being measured by the bolometer for any given wave-length and divided by the actual intensity of either spectrum for that wave-length, readily gives by the simple computation which will follow shortly, the magnitude of the rotation.

Of the two evident advantages resulting from this arrangement, one has already been mentioned. That is, the differential basis on which the measurement of rotations is placed, whereby the effect of small variations of the light source may be made negligible, and consequently far greater steadiness and certainty in the determination of small rotations secured. The second advantage results from the fact that the effect of any rotation is clearly doubled, since the increase of energy on one bolometer strip is accompanied by an equal decrease on the other, resulting in a doubled galvanometer deflection. Practically the only disadvantage results from the absorption of the calcite double image prisms, which prevents measurement beyond about $\lambda = 2.5\,\mu$. But in very many cases the absorption of the rotating substance itself precludes work beyond this wave-length. In certain other cases, too, particularly that of the magnetic metals, the interesting part of the curve is obtained well within this region of the spectrum, and indeed barely outside the limits of the visible part.

There are, moreover, a number of good features arising from the fact that many of the errors of adjustment, which are almost impossible to avoid, are rendered of negligibly small effect by this arrangement. The reason for this will appear after a brief discussion of the theory of the method.

Let $a$ be the angle which the plane of polarization of the incident radiation makes with the plane of transmission of the analyzer for the beam which goes to the upper half of the slit. Then if $I'$ represents the intensity for any wave length of the incident beam, the intensities of the two transmitted beams will be:

$$I_1 = k_1 I' \cos^2 \alpha \text{ to the upper half of the slit}$$

and

$$I_2 = k_2 I' \sin^2 \alpha \text{ to the lower half,}$$

where $k_1$ and $k_2$ are factors which take account of all losses which may occur to the two beams, due to any cause whatever, *e. g.*, narrowing of either half of the slit, absorption, etc.

Any small rotation of the plane of polarization $\delta$ will cause a relative change of intensity for the two beams of

$$dI = 2I'(k_1 + k_2) \sin \alpha \cos \alpha \cdot \delta.$$

Dividing by $I$, the intensity on either strip of the two are equal, or the mean if they differ slightly,

$$\frac{dI}{I} = 4\delta \frac{(k_1 + k_2) \sin \alpha \cos \alpha}{k_1 \cos^2 \alpha + k_2 \sin^2 \alpha}$$

or,

$$\text{if } \alpha = 45^\circ \ \delta = \frac{1}{4}\frac{dI}{I} \text{ radians or } \frac{45}{\pi}\frac{dI}{I} \text{ degrees.}$$

This shows that if $\alpha = 45^\circ$ a given rotation $\delta$ will be indicated by the same value of $dI/I$ whatever the values of $k_1$ and $k_2$. Furthermore, $\sin \alpha \cos \alpha$ being a maximum at 45°, a variation even as great as 4° either way changes it by less than 1 per cent, which means a correspondingly small change in the above factor if $k_1 = k_2$. If the two intensities are made equal, as is in general done to secure the compensating action explained above, $k_1 \cos^2\alpha = k_2 \sin^2 \alpha$, but the change in the factor for a variation in $\alpha$ of several degrees from 45°, is still barely a per cent.

The practical importance of these several facts is, that the factor by which the measured quantity $dI/I$ must be multiplied to give the angle of rotation, is practically a constant unless the variation of $\alpha$ from 45° is unreasonably large. This means that neither small errors in the adjustment of the polarizing arrangement, nor unknown absorptions or losses of radiation in any part of the apparatus, can have any appreciable effect on the accuracy of the results.

It is of interest to compare the possibilities for accuracy and sensitiveness of this bolometric method of measuring angles of magnetic rotation, with those of the ordinary visual methods. It is evident at once that the relative accuracies of the two will depend very largely on the magnitude of the rotation to be measured. For in ordinary polarimetry, rotations being measured as the difference between two settings of the analyzer, the probable error of the result is practically the same for small as for large rotations. On the other hand, in the present bolometric method, the probable error is by no means constant but is rather a fraction of the whole which is not many times greater for small than for large rotations. It is quite possible then, that, while the accuracy of visual observations may be very considerably greater for relatively large angles of rotation, *i. e.*, of several degrees, the bolometric method may excel in accuracy when the rotation is a hundred times as small.

A few figures will illustrate to what extent this is true. The accuracy of single settings with the most improved form of polarimeter is of the order of .01°. With the ordinary half shade arrangement the writer must confess to frequent discrepancies in successive measurements of several times this amount. On the other hand, in the bolometric method, a rotation of .01° would mean a ratio $dI/I$ of 1:1433 or a galvanometer deflection of one centimeter if the total energy incident on either strip corresponded on the same basis to 1433 cm. This, measured of course with reduced sensibility, is only one-half or one-third of what has readily been secured in practice in parts of the infra-red in the spectrum used, and a much smaller fraction of what would be available if the beam was undispersed. Hence it is evident that rotations several times smaller than could be detected visually, may, under proper conditions, be measured bolometrically. The possibilities for sensibility appear to be limited — supposing a rotating substance of not too great absorption — only by the intensity of the available source of light, and by the success with which this, as well as the bolometer and galvanometer are protected from various disturbing elements.

Of course the two methods are in no sense competitive, applying, as they necessarily do, to entirely different parts of the spectrum but it would seem that the bolometric method might perhaps find a special field of usefulness, outside of its natural application to rotatory dispersion determinations, in the detection of minute rotations. Unfortunately it is not applicable in general to the measurement of rotations due to naturally active substances, save in such a case as Brace's experiment on ether drift, where the effect to be measured is differential. In this case, however, it would probably be difficult to secure a naturally active substance sufficiently transparent in the infra-red to transmit enough energy for the measurements, through the great thickness required.

It is, perhaps, worth noting that the spectrometer and bolometer of this arrangement, taken alone, constitute a type of spectro-photometer applicable to infra-red comparisons of various light sources.

## THE MAGNETIC ROTATORY DISPERSION OF WATER IN THE INFRA-RED SPECTRUM.

Verdet[1] measured the magnetic rotation of water in a constant field, for the solar lines, *C* to *G*. Van Schaik[2] extended the determinations into the ultra-violet, finding that the rotation dispersion might be well represented by the expression $a\lambda^{-2} + b\lambda^{-4}$.[3] It was thought desirable in the present case to measure this dispersion for water in the infra-red, both in order to secure determinations for a larger spectral region over which formulæ might be tested, and also to find if the numerous infra-red absorption bands have any appreciable effect in modifying the form of the curve.

Using the foregoing method, measurements were made of the magnetic rotation of water for various infra-red wave-lengths, in a field of approximately 13,000 C.G.S. units. Because of its low rotatory power and high infra-red absorption, it is a peculiarly difficult substance to test in this way, but it was found that by using a rather thin cell — .616 cm. — a fairly consistent series of determinations could be made over the range of spectrum from $\lambda = .7\,\mu$ to $\lambda = 1.3\,\mu$, or as far into the infra-red as the ordinary dispersion has been determined.

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[1] Ann. Chim. Phys. (3), 69, p. 415, 1863.

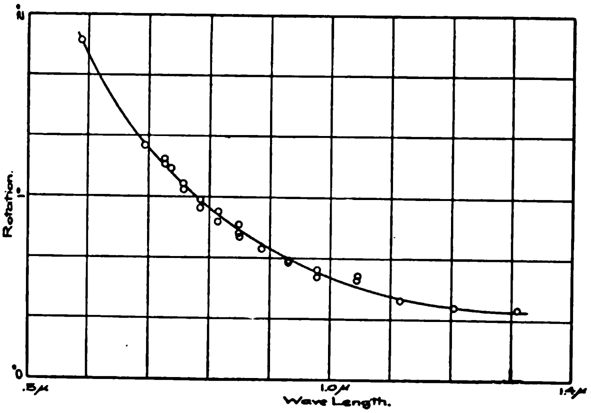
[2] Arch. Néerl., 17, p. 373, 1882.

[3] The careful experiments of Siertsema (Arch. Néerl. (2), 6, p. 825, 1901) give results in fairly good agreement with these.

A detailed description of the magnet and mirror system has already been given[1] and need not be repeated here, as this part of the apparatus was identical with that formerly used. The double image prisms of calcite and glass, used as polarizer and analyzer in the present case, were of 5 cm. and 4.5 cm. aperture, so that a rock salt prism with 8 cm. faces utilized practically the full beam transmitted. The differential bolometer had strips each 8 mm. by .5 mm. It proved in practice an extremely satisfactory instrument, for, as the balancing coils and slide adjustments were contained in the same case as the bolometer itself, "drift" was practically entirely eliminated.

The only correction necessary to the measurements was for the width in the spectrum of the bolometer strip and of the slit image, each .5 mm. wide. This for reasons previously explained,[2] was small, the calculated corrections varying from + 1.5 per cent. at $\lambda = .8\,\mu$ to − 1 per cent. at $\lambda = 1.3\,\mu$. Special tests with a wide slit, giving an exaggerated error, indicated corrections in general accordance with these. The effect of the thin cover glass ends of the cell was safely neglected, since preliminary trials indicated a rotatory dispersion curve for the glass very similar to that for the water, hence the effect of the ends would merely be to increase the equivalent thickness of the water cell 2 or 3 per cent.

In the following curve and table the results are summarized.



Magnetic Rotation of Water.

[1] Loc. cit.

[2] Loc. cit., p. 56.

The rotations plotted in the curve are half those actually measured — since the magnet current is reversed in the measurement — with the small correction above mentioned applied. The observed values given in the table are taken from the smooth curve and reduced to a scale which makes the rotation for sodium light unity. This point was determined by visual observations with a half shade polariscope.

TABLE I.

| Wave-length. | Observed Rotations. | Calculated Rotations. | |
|---|---|---|---|
| | | (2) | (1) |
| .589 μ | 1.000 | 1.000 | 1.000 |
| .70 | .695 | .676 | .683 |
| .80 | .514 | .496 | .510 |
| .90 | .389 | .389 | .399 |
| 1.00 | .312 | .315 | .322 |
| 1.10 | .254 | .259 | .263 |
| 1.20 | .220 | .220 | .220 |
| 1.30 | .201 | .193 | .181 |

The agreement of observed with calculated results is only fair, and hardly as satisfactory as in the case of carbon bisulphide. Results calculated from two slightly different formulæ are given. (1) is with the use of the formula given by Drude.[1]

$$\delta = \frac{1}{n}\left(\frac{a}{\lambda^2} + \frac{b\lambda^2}{(\lambda^2 - \lambda_1{}^2)^2}\right)$$

where $\lambda_1 = .127\,\mu$ is the wave-length of an ultra-violet absorption band. The constants, being determined for wave-lengths $.589\,\mu$ and $1.2\,\mu$ give $a = -.176$ and $b = +.582$, (2) uses the same formula modified by a term depending on the infra-red absorption band having its maximum at $\lambda = 3.02\,\mu$.

$$\delta = \frac{1}{n}\left(\frac{a'}{\lambda^2} + \frac{b'\lambda^2}{(\lambda^2 - \lambda_1{}^2)^2} + \frac{c'\lambda^2}{(\lambda^2 - \lambda_2{}^2)^2}\right).$$

The constants, determined for wave-lengths $.589\,\mu$, $.9\,\mu$ and $1.2\,\mu$ are $a' = -.517$; $b' = +.890$; $c' = +.804$.

It will be observed that there is only questionable advantage in favor of the second formula, which assumes the influence of an infra-red absorption band. This might perhaps be anticipated from the fact that the ordinary dispersion curve for water as determined by Rubens[1] as far as $\lambda = 1.256\,\mu$, does not show the effect of such an absorption band — in the early infra-red at any rate.

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[1] Lehrbuch der Optik, p. 403.

It is of interest to note that the theoretical formula proposed by Becquerel[2] and further worked out by Larmor,[3]

$$\delta = x\lambda \frac{dn}{d\lambda},$$

which fits very well in the case of carbon bisulphide,[4] fails entirely here, giving values for the rotation several times too large at $\lambda = 1.3\,\mu$.

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University of Wisconsin.

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[1] Wied. Ann., 45, p. 253, 1892.

[2] Comptes Rendus, Nov., 1897.

[3] Ether and Matter, p. 353.

[4] A discussion of this formula in its application to carbon bisulphide was unfortunately omitted in the previous paper. However at the suggestion of Professor Larmor it has since been tried and found to apply very well to $\lambda = 2.0\,\mu$ which is as far as the ordinary dispersion has been determined.

# THE IRREVERSIBILITY OF THE HEUSLER ALLOYS.

By Bruce V. Hill.

A LITTLE over a year ago the author, while making some experiments upon specimens of Heusler's magnetic bronzes (of manganese, copper and aluminium) found that these alloys are magnetically irreversible, but in a sense opposite to the irreversibility of the nickel-steels. A brief account of these experiments was published in this journal.[1] If an alloy of iron and nickel, containing up to twenty-seven per cent. of nickel, in the magnetic condition, be heated to from 700° to 750°C. it becomes unmagnetic. On being cooled it does not regain its susceptibility until the temperature has fallen to a point considerably below, in some cases several hundred degrees below, that at which the transformation took place during the heating. When heated a second time the metal remains magnetic until the original temperature of transformation is reached. If, starting at a high temperature with the steel in the unmagnetic condition, we descend to a moderate temperature, reheat to the starting point, cool again to a temperature lower than that reached in the first cooling, reheat and so on, we find that the susceptibility of the metal will, in general, be greater at room temperature, the lower the point to which it has been cooled.

With the magnetic bronzes, on the other hand, cooling to low temperatures, as in liquid air, has very little effect. The susceptibility depends rather upon the temperature from which the specimen has been cooled before the test is made. If heated to a temperature slightly above that of transformation, the susceptibility at room temperature is found to be smaller than when the alloy was first cast. On cooling successively from still higher temperatures the susceptibility at ordinary temperatures increases as the temperature from which the metal has been cooled rises.

It was further pointed out that, inasmuch as certain compounds of manganese possess a higher susceptibility than the corresponding ones of iron, we might expect to obtain the former in a strongly magnetic condition if a suitable alloy could be obtained. The magnetic bronzes are such alloys.

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[1] Physical Review, 21, p. 335, 1905.

According to the allotropic theory, which seems to be pretty well established, the ferromagnetic metals can exist in several allotropic forms depending upon the temperature. Only one of these forms is magnetic. In the case of many of the mechanical and physical properties, it is impracticable to study a substance at temperatures much above the ordinary. An indirect method must then be employed. When a metal is heated to a high temperature and suddenly cooled, passing in so doing a point of allotropic transformation, this transformation which would have occurred during a slow cooling, is hindered or perhaps almost wholly prevented by the rapid cooling. This is made use of in studying the conditions existing in alloys at high temperatures. In the case of the steels, for example, when the metal has been heated to a high temperature and suddenly cooled, we consider that we have it before us in the condition in which it was at the high temperature. If this were strictly true in all cases we might expect to find the magnetic bronzes magnetic at high temperatures since their susceptibility is greater the more elevated the temperature from which they have just come. Without experiment it is impossible to say whether this will be true or not. We naturally think of these metals as being always unmagnetic above the temperature of transformation. Dr. D. K. Morris found, however, that iron becomes unmagnetic at a temperature between 700° and 750°C, but regains its susceptibility to a slight extent between 800° and 1,000°C. I thought it worth while therefore to test some further specimens of the Heusler alloy in order to determine the magnetic condition of the metal between the points of transformation and fusion, that is between 250° and 1,000°C.

Four alloys were prepared. They were made by melting a copper-manganese alloy with aluminium. An ordinary gasoline furnace was used and the melts made under borax glass as a flux. The copper-manganese was obtained from one of the best firms in the country and was supposed to contain thirty per cent. of manganese. The upper portion of the pig of metal contained a considerable amount of slag. The analyses showed the per cent. of aluminium to be so nearly that of the mixture before melting, while that of the manganese was so much below what was expected, that it is fair to assume that the manganese was burned out in the manufacture of the original copper-manganese alloy. The analyses, for which I am indebted to Professor McFarland of the Department of Chemistry of the University of Kansas, are as follows:

| Alloy Number. | Copper. | Aluminium. | Manganese. |
|---|---|---|---|
| 1 | 74 | 22 | 4 |
| 2 | 65 | 34 | 1 |
| 3 | 65 | 32.5 | 2.5 |
| 4 | 63 | 34.3 | 2.7 |

The discoverer of these bronzes, F. Heusler[1] has recently published an account of experiments upon certain alloys rich in copper which are, nevertheless, very highly magnetic and which are malleable.

The apparatus used in the testing of my alloys was that described in the previous note upon this subject. The temperatures were measured with a platinum — platinum 10 per cent. rhodium couple. The curves showing the relation between the intensity of magnetization and the temperature for alloy No. 1 during three successive cycles are given in the figure. The field throughout the tests was 38 C.G.S. units. The curves of decreasing intensity, that is of increasing temperature, are indicated by the arrows immediately below them.

Starting at room temperature the intensity, $I$, is 175. It falls rapidly as the temperature rises, becoming zero at 320°C. The heating was continued up to 750°, the point $C$ in the figure. On cooling the curve returns to the point $D$ where $I = 47$. The temperature was now raised to 890°C., the point *E*. This time the return was to *F*, $I = 53$. Being heated the third time to 520°C. and cooled to room temperature the rod showed an intensity $I = 44$.

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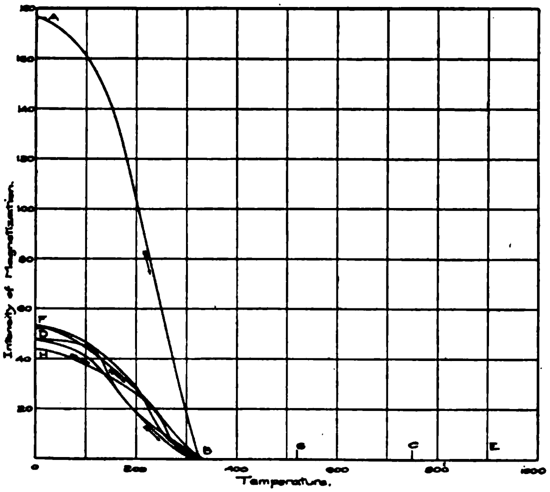
[1] F. Heusler, Beiblaetter, 29, 1238, 1905, or Schriften d. Marburger Gesell. J. A. Fleming and R. A. Hadfield have published tests upon some of these alloys but nothing distinctly new is given.

Professor A. Gray, of Glasgow (Proc. Roy. Soc., Sect. A., 77, p. 256, March 6, 1906), has also tested two specimens of these bronzes finding them like those of the other experimenters.



Alloy No. 2 was unmagnetic as cast. Pounding or jarring produced no noticeable effect. The rod was then heated successively to 325°, 490° and 810° C., but it remained unmagnetic throughout. When broken in a mortar the fragments were magnetic. It melted at 975° C.

Alloy No. 3 showed a course similar to that of No. 1. When cast the intensity, *I*, was 123. Transforming at 300° it was heated to 320° and allowed to cool. *I* attained a value of 128. The second heating was to 500°, after which the intensity at room temperature was 48. The third heating was to 730°, after which the value of *I* was 41. The fourth heating was to 890°, the intensity becoming $I = 44$ at room temperature.

Alloy No. 4 was tested at room temperature as cast and after being heated to the same series of temperatures as was No. 2. The results were: As cast $I = 41$, after heating to 325° $I = 41$, after heating to 490° $I = 14$ and after heating to 810° $I = 63$.

The data for these four alloys, as well as for the one described in the previous paper, which will be called No. 5, are brought together in the table. $H = 38$ for the first four and 85 for the fifth.

| | | | | | |
|---|---|---|---|---|---|
| Alloy No. 1 | As cast | 520° | 750° | 890° C. | |
| | $I=175$ | 44 | 47 | 53 | |
| Alloy No. 2 | As cast | 325° | 490° | 810° C. | |
| | $I=0$ | 0 | 0 | 0 | |
| Alloy No. 3 | As cast | 320° | 500° | 730° | 890° C. |
| | $I=123$ | 128 | 48 | 41 | 44 |
| Alloy No. 4 | As cast | 325° | 490° | 810° C. | |
| | $I=41$ | 41 | 14 | 63 | |
| Alloy No. 5 | As cast | 368° | 500° | 650° | 850° C. |
| | $I=311$ | 267 | 27 | 90 | 155 |

From these results we see that, in general, the susceptibility of the alloy at room temperature decreases as the temperature to which it has been heated rises, up to a certain point, beyond which the intensity increases again. Nos. 4 and 5 show these characteristics more pronouncedly than the others. All the alloys, with the possible exception of No 3 in the first cycle, show them however, though in the first four, those of low manganese content, they are not so marked.

We see also from the figure that the alloys do not regain their magnetic properties at the higher temperatures. If we assume that the molecular state of the metal is in great measure that naturally stable at the higher temperature due to the retardation or non-occurrence of certain allotropic changes, then we must suppose that there are different molecular arrangements of the metals constituting the alloy at different temperatures. The relations existing at high temperatures allow the transformation of the manganese from the *beta* to the *alpha* state to take place more completely than in those molecular groupings existing at lower temperatures. The temperature-intensity cycles are irreversible, but cannot be repeated as with the irreversible nickel-steels. This is probably due, in part at least, to the fact that the time during which the metal is held at a certain temperature plays a great part in determining the nature of its subsequent properties, as shown originally by Messrs. Haupt and Stark[1] and by E. Gumlich[2]. By casting a number of rods from the same crucible, and thus avoiding the repeated heating of the same rod, some additional information might be gained.

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[1] Marburger Schriften, Bd. 13, 1904.

[2] Ann. d. Phys., 16, p. 535, 1905.

While the experiments upon these bronzes may have brought us very little nearer to an understanding of the phenomenon of magnetism, they seem to make it evident that we have here to do with a molecular and not an atomic property.

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# NOTE ON THE VIBRATION GALVANOMETER.

By Roy T. Wells.

IN Annalen der Physik, Bd. 4, Heft 3, March, 1901, p. 439, Max Wien described an apparatus very considerably more sensitive than a telephone, for the detection and measurement of harmonic electromotive forces and currents of small amplitude.

The writer sometime since had occasion to investigate with such an instrument

(*a*) Its accuracy of tuning, that is the variation of its amplitude of motion when acted upon by an electromotive force of constant amplitude and frequency, the natural period of the instrument being varied from less than to more than that of the impressed electromotive force.

(*b*) The way in which the magnitude of the instrumental reading varies with the amplitude of an impressed electromotive force of fixed frequency, with which it is in resonance.

An electrically driven tuning fork was arranged to open and close a circuit consisting of battery and coil of wire, giving an intermittent, unidirectional current in the coil. A second coil in inductive relation to the first thus had induced in it an alternating electromotive force, and was connected in series with a piece of German silver wire stretched along a scale, there being accordingly a non-harmonic alternating current in the stretched wire, of almost perfectly fixed frequency.

(*a*) The galvanometer terminals were kept connected to certain fixed points of the stretched wire, so that when the galvanometer key was closed a constant current passed through its coil. The free length of the suspending wire was varied by small increments and the corresponding amplitude of vibration noted.

The results are given in Table I. and plotted in Fig. 1, the variables in each case being free length of wire in centimeters and amplitude of vibration as measured on a scale in the eyepiece of the observing telescope.

From the table it is seen that for this wire and frequency a free length of wire of 11.94 cm. brought the needle into resonance with the impressed electromotive force. From the amplitudes with free lengths of 11.90 and 11.94 cm. it is seen that a reduction of the free length of .34

TABLE I.

| Free Length. | Amplitude. | Free Length. | Amplitude. |
|---|---|---|---|
| 10.16 | 2.750 | 12.95 | 6.875 |
| 10.41 | 2.750 | 13.21 | 6.875 |
| 10.67 | 4.125 | 13.46 | 5.500 |
| 10.92 | 4.125 | 13.71 | 5.500 |
| 11.18 | 2.750 | 13.96 | 4.125 |
| 11.43 | 4.125 | 14.13 | 4.125 |
| 11.69 | 6.875 | 14.23 | 4.125 |
| 11.90 | 8.250 | 14.40 | 5.500 |
| 11.94 | 137.500 | 14.58 | 4.125 |
| 12.19 | 13.750 | 14.75 | 4.125 |
| 12.45 | 10.800 | 15.13 | 4.125 |
| 12.70 | 8.250 | | |

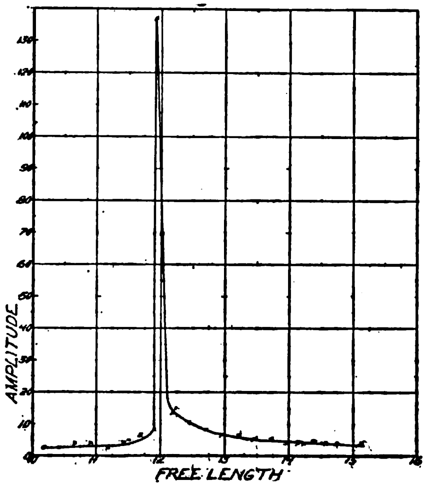

Fig. 1.

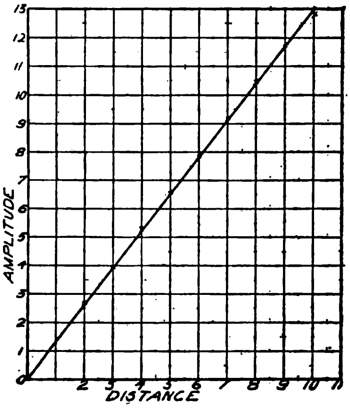

Fig. 2.

per cent. and hence a reduction of .17 per cent. in the natural period of the needle reduces the amplitude of vibration by 90 per cent. This shows that to use such an instrument satisfactorily it must be accurately tuned and supplied with an electromotive force almost perfectly constant in frequency.

(*b*) The instrument was tuned to the tuning fork, and its terminals connected to points on the stretched wire at distances apart increasing by regular increments, the amplitude of vibration being noted in each case. The results are given in Table II. and plotted in Fig. 2, the variables in each case being distance in centimeters between points of galvanometer connection and amplitude of vibration.

TABLE II.

| Distance. | Amplitude. | Distance. | Amplitude. |
|---|---|---|---|
| 1 | 1.32 | 6 | 7.84 |
| 2 | 2.68 | 7 | 9.16 |
| 3 | 3.93 | 8 | 10.48 |
| 4 | 5.30 | 9 | 11.71 |
| 5 | 6.58 | 10 | 12.80 |

These results show that the amplitude of vibration is very closely proportional to the impressed potential difference.

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# NEW BOOKS.

*Ions, Electrons, Corpuscles.* Memoires reunis et publié par HENRI ABRAHAM et PAUL LANGEVIN. Paris, Gautier-Villars, 1905. Pp. xvi + 1138.

This important collection of papers, which constitutes the second series of memoirs issued by the *Société Française de Physique*, deals, as the title indicates, with the phenomena upon which the modern conception of the existence and function of the electrified particle is based. The charged corpuscle has become a fundamental quantity in our newer theories concerning matter and electricity and the contributions gathered together and rendered easily available in this compilation represent an important epoch in physics.

The work was originally undertaken on behalf of the Société de Physique by the late Professor Potier and to his memory the present volume is dedicated by its editors Professors Abraham and Langevin.

The literature of this new portion of the science of physics is already so large as to compel the exclusion, even from so voluminous a collection as this, of many papers of interest and significance. While some readers will regret the entire omission of the work of various contributors to our knowledge, as for example that of Barus and of Child, every one will be glad that place was found for the early papers of such pioneers as Plücker, Hittorf, Crookes, Coulier, Giese and Hertz.

In these days when men of science, whatever their nationality, make daily use of English, French and German in about equal proportions it would seem as though all of the papers of this collection might well have been reprinted in the original. The foreign memoirs have however been rendered into French and the surprising skill of the French scientific translator, which often enables him to preserve the thought of an author and to give it a more complete and perfect expression is pleasingly manifest in the various versions prepared by M. M. Langevin, Salles, Bloch, Gallotti, Benard, Buirson, Lugol and Moulin. The very important summary of the work of Lorentz was prepared by the author himself.

In preference to either the chronological order or the arrangement of material according to subjects, the editors have placed the various papers alphabetically by authors, a plan awkward for the few who may wish to read the work through consecutively but which greatly facilitates the use of the collection as a book of reference.

E. L. N.

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